

Studies on Synthesis, Stability and Dye incorporation into Large Pore Molecular Sieves

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For Trish

and in memory of Barrie

The work presented in this thesis is the original work of myself, except where specific reference is made to other sources. It has not been submitted, in whole or in part, for any other degree.

Abstract

The work described in this thesis is concerned with the synthesis, stability and dye incorporation into large pore molecular sieves, in particular looking at the ultra-large pore aluminophosphate molecular sieve VPI-5.

The synthesis of VPI-5 was carried out with two types of system:

- i) Gels templated with the amine di-n-propylamine.
- ii) A clear solution “organic-free” system using a water soluble aluminium phosphate hydrochloride ethanolate (APHE) precursor.

High purity yields of VPI-5 were obtained by optimisation of both systems. Analysis of the products produced by the different synthesis routes gave evidence that the aluminophosphate H1 and VPI-5 are very closely related.

By the addition of polyethylene glycol to APHE systems large single crystals (10-20 μm wide by 250-1000 μm long) of VPI-5 were synthesised for single crystal X-ray diffraction studies.

The thermal stability of VPI-5 was thoroughly investigated and the apparent activation energy for the conversion of VPI-5 (synthesised with di-n-propylamine) to $\text{AlPO}_4\text{-8}$ was determined as 80 kJ mol^{-1} .

Methods for maximising uptake of dyes into VPI-5 were systematically studied, along with the effects of sorbed dyes on the thermal stability of VPI-5. The use of vessels made from fluoroethylene polymer tubing was found to give high dye uptakes of dyes (up to 4% w/w) in a reproducible manner by allowing controlled escape of water. High uptakes of some dyes were found to prevent the transformation of VPI-5 to $\text{AlPO}_4\text{-8}$. Encapsulation of dye within VPI-5 was shown to be capable of increasing the photostability of the dye.

Dye sorption into faujasite materials with differing Si / Al ratios was investigated. A water sensitive solvatochromic complex was formed when the dye waxoline yellow RPFW was sorbed into the hydrogen form of dealuminated zeolite Y.

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Chapter 1

Introduction

1.1 General

There is a wide range of materials which can be defined as molecular sieves. The term was coined by McBain in 1932 [1] and refers to any solid materials, crystalline or amorphous, which have the ability to differentiate between molecules on the basis of their size. The work described in this thesis is concerned solely with the use of various crystalline molecular sieves, mainly the aluminophosphate material VPI-5, but also the zeolites X, Y, and ZSM-5, and the all-silica molecular sieve silicalite. What they all share, in common with other crystalline molecular sieves, are regular crystalline structures which consist of uniform pores linked to form channels or cavities within the crystals. Molecular sieves owe their properties to their structure, especially their pore size, and also to their elemental composition. These areas will be discussed in more detail later. The first crystalline molecular sieves to be discovered were the zeolites, which are aluminosilicates. This introduction will start off by looking at zeolites and then show how research on zeolites led to the discovery of other classes, including the all-silica and the aluminophosphate molecular sieves.

1.2 Zeolites

Zeolites are aluminosilicate materials, some of which occur naturally. Natural zeolites were first recognised in 1756 by the Swedish mineralogist Cronstedt: He noticed that crystals which he had found violently gave off water when heated [2]. For this reason he named the new minerals zeolites after the Greek words for “boiling stone”.

1.2.1 Structure

Zeolites have been defined as naturally occurring crystalline aluminosilicates characterised by three-dimensional framework structures. Their frameworks are composed of linked tetrahedra of SiO_4 and AlO_4 . The non-oxygen tetrahedral

framework elements are often referred to as 'T-atoms', without specifying whether they are aluminium or silicon. In representing molecular sieve structures the accepted method is for a vertex to indicate a T-atom whilst a line represents the T-O-T bond, with an oxygen atom at or near its mid point.

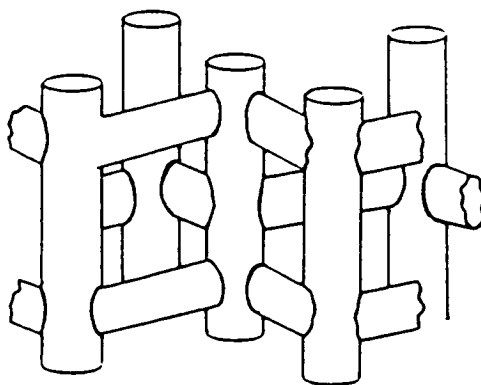
The framework structures provide 1-, 2-, and 3-dimensional channel systems. In some cases the structure may have more than one channel system, and in such systems the channels are usually interconnected, an example of this is ZSM-5 (Figure 1.1). In addition to well defined channels, some frameworks have large supercages, accessed by smaller windows. The best example of this is the faujasite framework where the supercage has a diameter of approximately 13Å and a window size of 8Å. The structure of faujasite is shown in Figure 1.2.

An important parameter of any zeolitic framework is the Si / Al ratio, which can range from one (i.e. equal amounts of Si and Al) to several thousand for materials which can be virtually considered as all-silica. The importance of the aluminium is that it leads to a negatively charged framework: each Al^{3+} atom requires one charge-balancing univalent cation [3]. These charges need to be balanced and this is normally done by small inorganic cations such as sodium, which sit in the void space. This in turn affects the other pore contents, which usually includes water.

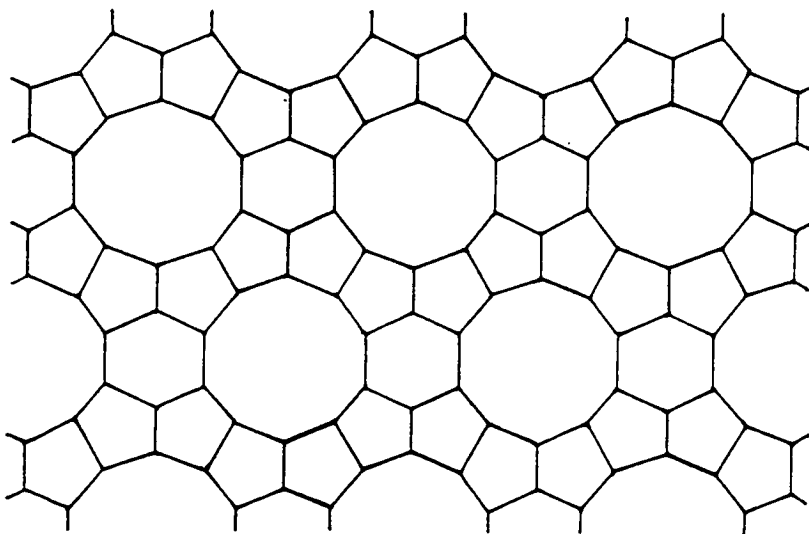
It is not normally possible to have Al-O-Al bonds for tetrahedrally co-ordinated aluminium and therefore the Si / Al ratio cannot be less than one. This avoidance of Al-O-Al bonds is known as Lowenstein's rule [4] and is rationalised on the basis that clusters of negative charge are less stable than isolated negative charges. Zeolites X and Y both share the faujasite structure, but are distinguished by differing Si / Al ratios, zeolite X has a ratio of approximately 1 - 1.5 [5] whilst zeolite Y is the name used for faujasite structures with ratios higher than 1.5.

There are many zeolites and molecular sieves which are isostructural, differing only in areas such as Si / Al ratio or in elemental composition. Each unique composition has its own name, as conferred by the discoverer. However the structure types have been designated 3 letter codes by the International Zeolite Association (IZA). For example zeolites X and Y share the FAU structure type. A full list of structure types and their designated letters can be found in the 'Atlas of Zeolite structure types' [6].

Figure 1.1 Zeolite ZSM-5

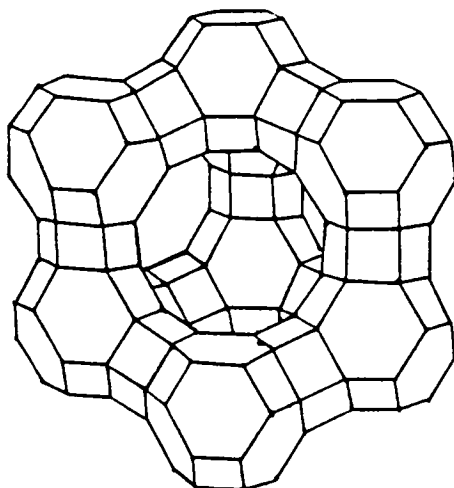


a) Channels of zeolite ZSM-5



b) A sheet projection of the pore openings of ZSM-5. Each vertex represents a tetrahedral site, the fourth bonds (not shown) connect the layer to the rest of the framework.

Figure 1.2 The framework of faujasite



This figure shows the nature of the zeolite cages.

1.2.2 Synthesis

Natural zeolites are synthesised hydrothermally, that is from hot aqueous systems which contain the necessary components [5]. It is the reproduction of these conditions in the laboratory which has led to the synthesis, not only of analogues of the natural zeolites, but also to totally new structures. There were reports as early as 1862 of the successful synthesis of levinite (levyne), however the lack of definitive identification data means that many early reports cannot be substantiated.

Detailed systematic research into zeolites began in the early 1940s when Barrer and co-workers in Britain and the United States commenced research. As well as synthesising analogues of natural zeolites, Barrer reported the first synthesis of novel synthetic phases [7]. The method used by Barrer involved a hydrothermal recrystallisation of analcime at relatively high temperatures (180 - 220°C) and correspondingly high pressures. The major breakthrough in zeolite synthesis was reported by Milton and co-workers at Union Carbide in the late 50's and is known as the gel synthesis method. It involves the hydrothermal crystallisation of an inhomogeneous aluminosilicate gel, it is the most commonly used, and the most

successful technique. The first new zeolite obtained by this method was zeolite A, synthesised by Breck and co-workers in 1956 [8]. Most gels contain an organic compound, usually an amine or a quaternary ammonium salt which acts as a template or a void filler, though for any given synthesis it is usually not clear which role it takes.

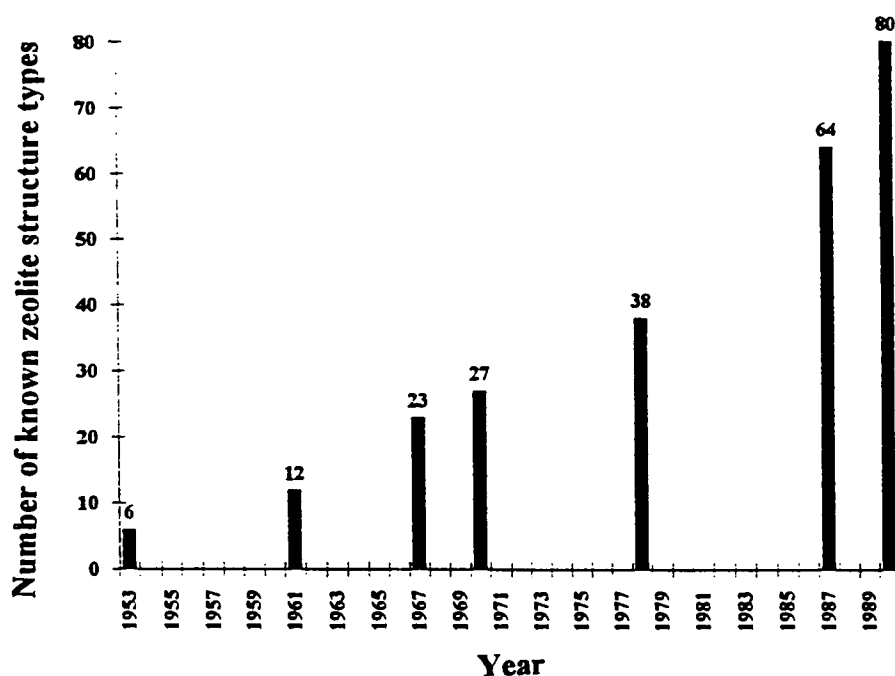
The synthesis of new structures is influenced by many aspects of the basic gel chemistry, such as gel composition, pH, temperature, digestion time, starting materials, etc. [9]. Thus the full mechanism of crystallisation is not yet fully understood and much synthesis research is more concerned with producing new commercially valuable materials than in trying to elucidate the exact mechanisms of synthesis. What is known, however, is that zeolites are non-equilibrium phases, this means that they are metastable and can convert to a more stable species [5]. Ostwald's law of successive reactions is followed which states that the first phase produced is consumed and replaced by a thermodynamically more stable second phase and so on until the most stable phase is formed [10].

The above applies to the synthesis of all other crystalline molecular sieves as well and often means that there is a relatively small window of reaction conditions in which a pure form of the desired phase can be synthesised. Successive phases tend towards denser, non-molecular sieve materials so that, for example, the most stable phase to be formed from SiO_2 is quartz.

In the early 1970s a new series of highly siliceous zeolites were reported by Mobil research workers and were named the ZSM series. One of the earliest members of the series, called ZSM-5 [11], is of particular importance for its catalytic applications. In 1977 an all-silica analogue of ZSM-5, named silicalite, was reported [12,13]. Silicalite is regarded by some as the end member of the ZSM-5 series and thus illustrates a problem which can be encountered in zeolite nomenclature: identical or closely related materials prepared in different laboratories are often given different names. The IZA framework name for these materials is MFI [6].

There are still a large number of potential frameworks to be synthesised and research continues apace: in 1980 Sand reported that only 10 % of all possible polymeric configurations had been discovered [14]. Figure 1.3 shows the development of the number of known zeolite structures [15]. There have even been attempts to synthesise zeolites in space [16]. Many molecular sieves form as very small crystals and so the introduction of more powerful analytical techniques such as crystal studies with synchrotron radiation [17] enables unknown structures to be solved.

Figure 1.3 The development of the number of known zeolite structure types [6]



In naturally occurring minerals isomorphous substitution is common and it was therefore an obvious development of zeolite science to carry out similar substitutions. There have thus been many attempts to synthesise molecular sieves which are based on different framework elements. One area of research looked at the synthesis of aluminophosphate materials and the announcement of the first aluminophosphate molecular sieves was made in 1982 by Flanigen and co-workers at Union Carbide [18].

1.3 Aluminophosphate molecular sieves

1.3.1 General

In nature AlO_4 and PO_4 tetrahedra yield a variety of neutral frameworks, amongst them berlinite (an analogue of quartz), variscite, metavariscite, and an analogue of tridymite [19], and so it was natural to investigate the synthesis of aluminophosphates [20,21,22], leading on to investigations into the possibility of synthesising aluminophosphate molecular sieves.

As was said, in 1982 workers at the Union Carbide laboratories reported the discovery of a whole series of crystalline microporous materials based on frameworks of alternating AlO_4 and PO_4 tetrahedra [18], which they called AlPO_4 s. Each structure type then has a number, based presumably on the order in which they were discovered, e.g. AlPO_4 -5, AlPO_4 -11. These structure type numbers are unique to aluminophosphate based molecular sieves synthesised at Union Carbide and have no historic significance; for example ZSM-5 and AlPO_4 -5 do not have the same structure. Aluminophosphate molecular sieves synthesised elsewhere are not named according to this system.

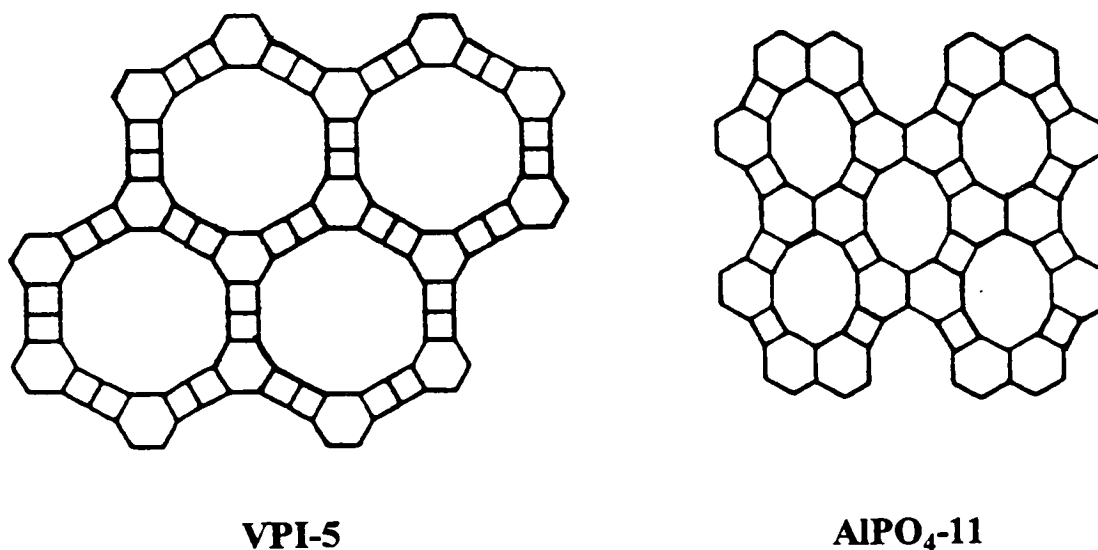
As with zeolites Al-O-Al linkages are disallowed by Lowenstein's rule, whilst P-O-P linkages are unlikely when P is tetrahedral as it would place two positive charge centres in close proximity to one another. Because of this, strict alternation of Al and P throughout the frameworks is expected and found. This then means that all of the frameworks are composed of rings which contain an even number of T-atoms.

The initial report of Union Carbide was of nine different AlPO_4 frameworks, within four years this had grown to 24 and there are now numerous synthetic aluminophosphates. These include structures related to those of zeolites (e.g. AlPO_4 -34 has the same topology as chabazite (CHA)), as well as many novel structures (e.g. AlPO_4 -11 (AEL)). It also turned out that some materials made previously were microporous, e.g. the aluminophosphate H2 synthesised by D'Yvoire [20,23].

1.3.2 VPI-5

Initially the pore sizes of aluminophosphates varied from 3 to 8 Å, thus were similar to those of zeolites. The size was dramatically increased by the discovery in 1988 of VPI-5, which turned out to be an aluminophosphate molecular sieve with 12 Å pores, formed by 18 T-atom rings. The large size of VPI-5 pores was clearly demonstrated [24] when VPI-5 successfully adsorbed triisopropylbenzene, a molecule not sorbed by most molecular sieves and only very slowly sorbed by zeolite Y. Structure determination confirmed the size as 12 Å [25]. Larger pores increase the range of molecules which can be accommodated inside a molecular sieve and so such structures are continually sought after. Figure 1.4 shows the structure of VPI-5 in comparison with that of $\text{AlPO}_4\text{-11}$, which has pore openings of 6.3 x 3.9 Å [6].

Figure 1.4 The structures of VPI-5 and $\text{AlPO}_4\text{-11}$



There has been a huge interest in VPI-5, marked by an explosion in the number of research papers about it. These have reported many fascinating features of this material some of which are briefly described below.

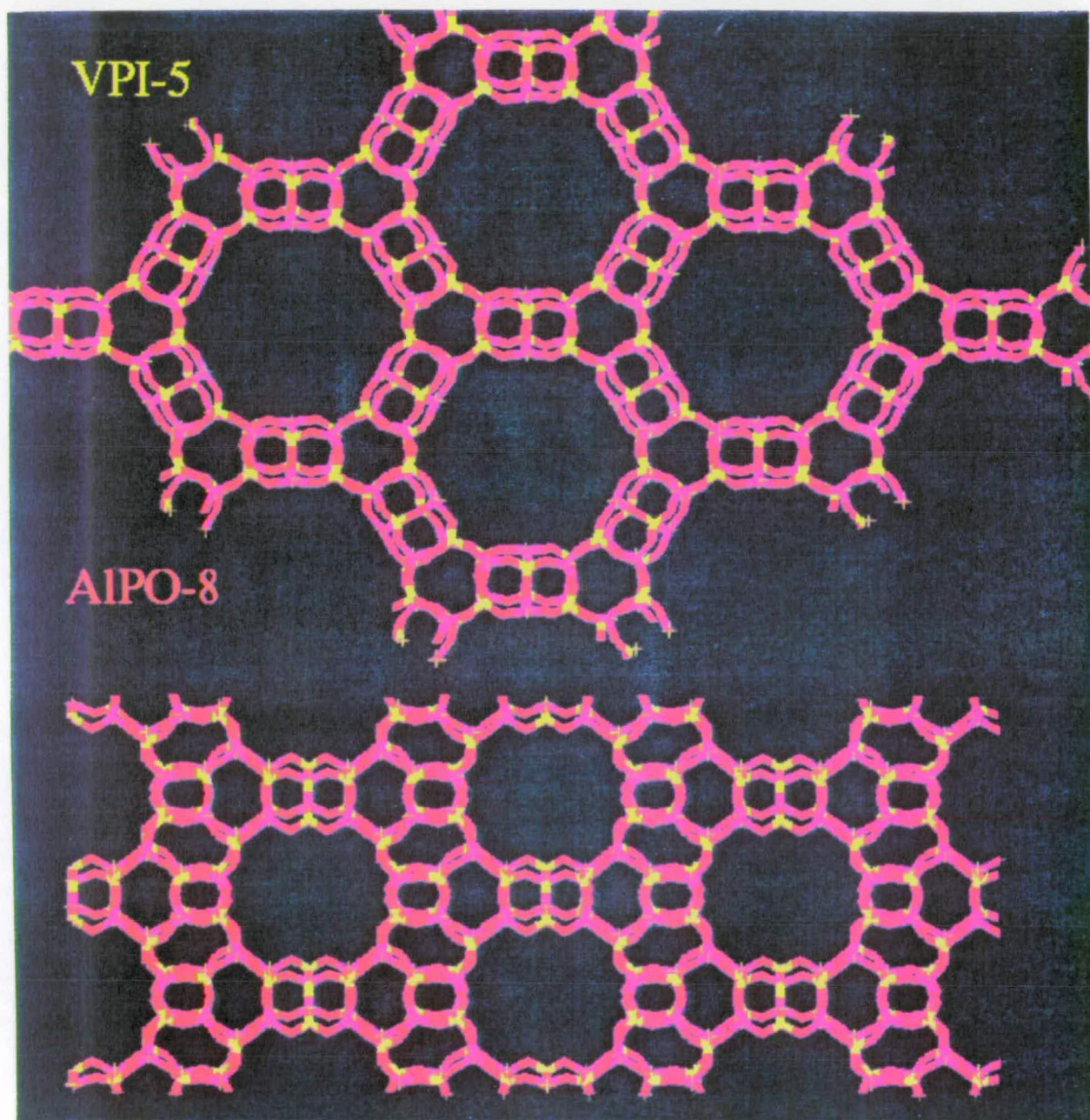
It has been shown that VPI-5 can be synthesised using a variety of organic additives, none of which are found inside the crystalline product to any great extent [23,26]. This suggested that their role was not the same as in most other molecular sieve syntheses, i.e. as templates or void fillers. A possible role for the additives was as pH controllers, which implied that it might be possible to dispense with them. Two routes have indeed been reported by which VPI-5 was successfully synthesised from solutions which did not contain organic additives [27,28,29]. The successful synthesis of VPI-5 from such solutions lent much to a debate about whether or not VPI-5 is the same as the aluminophosphate H1 [20]. This topic is discussed in detail in Chapter 3.

It was shown that VPI-5 is an aluminophosphate hydrate [30], that is to say it contains structural water, attached to some framework aluminium atoms so that they are octahedrally co-ordinated. This turned out to be fairly common in aluminophosphates [31,32], although it has not been seen in zeolites. Less common was the fact that the rest of the water sorbed into the channels of VPI-5 was found to be structured such that it formed a triple helix [33].

A final feature of note on VPI-5 is that it can undergo a solid-state transformation when heated, to form another molecular sieve: $\text{AlPO}_4\text{-8}$ [34]. $\text{AlPO}_4\text{-8}$ was first reported in 1982, in the original AlPO_4 patent [18], although its structure was not determined until 1990 [35]. The conditions required for the transformation of VPI-5 into $\text{AlPO}_4\text{-8}$ are discussed in detail in Chapter 4. Figure 1.5 shows the structures of VPI-5 and $\text{AlPO}_4\text{-8}$.

There has since been a report of an aluminophosphate with a larger pore size than VPI-5. JDF-20 was reported in 1992 [36] and contains elliptical pores and channels which are circumscribed with 20 T-atoms, although the pores are slightly blocked by terminal hydroxyls which project into them.

Figure 1.5 The structures of VPI-5 and $\text{AlPO}_4\text{-8}$



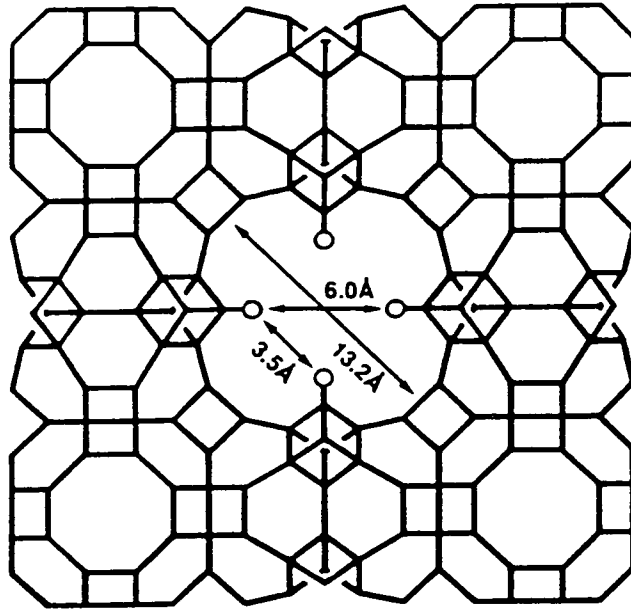
1.3.3 Substituted aluminophosphate molecular sieves

Not only have many different AlPO_4 structures been synthesised, but many elements have been substituted in place of either aluminium or phosphorous, e.g. silicon, iron, cobalt, zinc, and gallium [37,38,39,40]. There are natural precedents for this in that most phosphate minerals which contain aluminium also contain other cations such as Ca, Fe, or Mg [19]. The synthesis of structures with wide pores was known to be possible since a widespread ferric phosphate, cacoenite, was shown to be microporous and had its free pore diameter calculated as 14.2\AA [41]. As well as producing analogues of most AlPO_4 s, the use of other framework elements has led to the synthesis of novel structures, most notably cloverite, a gallophosphate with 20 T-atom pores leading into supercages with body diameters of $29 - 30\text{\AA}$ [42]. Like JDF-20, cloverite has terminal hydroxyls projecting into the pore: it is these that gave the structure its name for they cause the pore to be shaped like a four-leafed clover. Figure 1.6 shows the structures of cloverite and JDF-20.

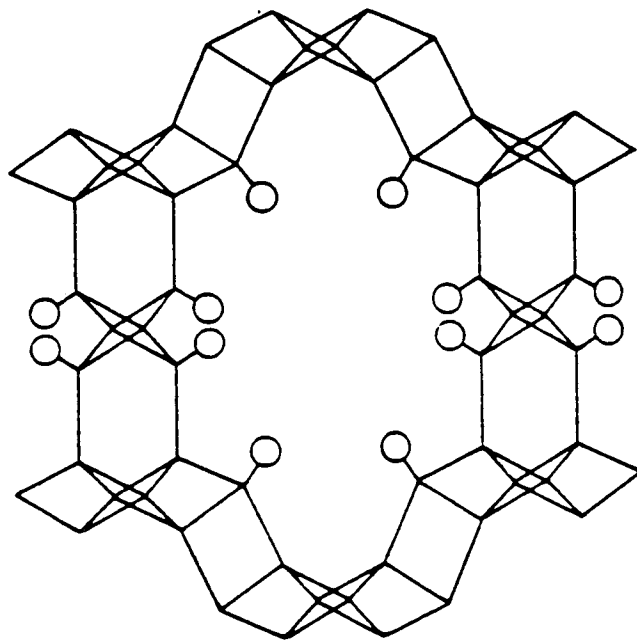
Recently a novel synthesis process was reported in which tube like structures of aluminophosphates or substituted aluminophosphates were created in the presence of liquid crystals [43,44]. These materials contained pore sizes of around $50-90\text{\AA}$, depending on the liquid crystal which was used. This is a huge leap in size over previously reported molecular sieves, although it is yet to be seen whether these can be classified as true molecular sieves.

Figure 1.6 The structures of cloverite and JDF-20

Note the hydroxyl groups pointing into the pores.



cloverite



JDF-20

1.4 Properties and Uses

It is the open frameworks of molecular sieves which are the key to their importance, for they allow selective uptake of molecules, and can also constrain sorbed molecules into particular configurations which allow further selectivity in how the molecule reacts or behaves.

1.4.1 Properties

For molecular sieving the most important physical characteristic is the pore diameter. As has been said, the channel sizes are determined primarily by the number of atoms in the rings which make up the framework. Described in terms of the T-atoms, the channels can range in size from 6 T-atoms (e.g. sodalite), through 12 T-atoms for the largest zeolites, to 18 T-atoms for VPI-5, with respective diameters of 3, 8, and 12 Å. The temperature of sorption is also important, as vibration in the T-O-T bonds increases with temperature and may allow larger molecules to enter the framework.

The pore size also depends on the actual shape of the ring, for example zeolite A has an eight T-atom ring with a diameter of 4.1 Å, whilst chabazite, also with an eight T-atom ring, has a diameter of 3.8 Å because it is slightly puckered.

It is difficult to accurately quantify the surface area of molecular sieves, though it is generally accepted that the surface area is typically about 1 % external and 99 % internal. The difficulty in measuring the surface area arises because the pore diameter places constraints on sorbed molecules sitting side by side in a pore. Thus when surface area determinations are performed (e.g. by the BET method) the results may be invalid because the internal surface is not necessarily completely covered. Therefore, in molecular sieve science it is much more normal to talk about void volume. This depends only upon the amount of pore structure which is accessible to sorbate molecules. It is calculated by measuring the maximum uptake of sorbate in the pore system and then calculating the equivalent sorbate volume. Table 1.1 lists the void volumes of three AlPO_4s , all with unidimensional channels but of different sizes. Also detailed are other important features of their structures which affect what molecules they can adsorb.

Table 1.1 Properties of three AlPO_4 s derived from crystal structures [45].

Molecular Sieve	Framework Density, $\text{TO}_2 / 1000 \text{ \AA}^3$	Free diameter of pore ^a / \AA	Total void volume ^b / $\text{cm}^3 \text{ g}^{-1}$	Void volume of the unidimensional channel ^b / $\text{cm}^3 \text{ g}^{-1}$
$\text{AlPO}_4\text{-11}$	19.1	6.3 x 3.9 elliptical	0.134	0.080
$\text{AlPO}_4\text{-5}$	17.5	7.3 circular	0.180	0.147
VPI-5	14.2	12.1 circular	0.310	0.255

^aBased upon an oxygen radius of 1.30 - 1.35 \AA .

^bAssumes a density of $2.6 \pm 0.05 \text{ g cm}^{-3}$ for the aluminophosphate framework.

The framework density (FD), listed in column 2, is related to the pore volume, the lower the framework density the higher the pore volume. For zeolite frameworks the observed FDs range from 12.5 to around 20.5 $\text{TO}_2 / 1000 \text{\AA}^3$ [6].

The frameworks of AlPO_4 s are neutral and are constrained to an Al / P ratio of 1 however, as has been said, those of zeolites can have variable Si / Al ratios and they are charged due to the Al, which means that there are cations present. As aluminium content rises there is an increase in the framework negative charge which requires an increased cation concentration to balance it. Since the cations can be ion-exchanged this leads to increasing ion exchange capacity. These features account for many of the properties and uses of zeolites.

A major change which has been observed as the Si / Al ratio changes is in the hydrophobicity of the materials. Chen showed that for synthetic mordenite samples the degree of hydrophobicity was dependent upon the Si / Al ratio [46]. The rationalisation of this is very simple: a polar water molecule is attracted to the charge centres in the framework, as the amount of aluminium in the framework decreases so the number of charge centres decreases. If the framework is composed only of silicon tetrahedra there is no framework charge and therefore extreme hydrophobicity, e.g. silicalite.

The charge balancing cations can affect the window size, for example in zeolite A the replacement of Na^+ ions with Ca^{2+} ions widens the aperture size whilst their replacement with K^+ ions reduces the diameter. Another feature associated with cations is that when they are hydrogen ions the negatively charged aluminium is associated with a catalytically active site.

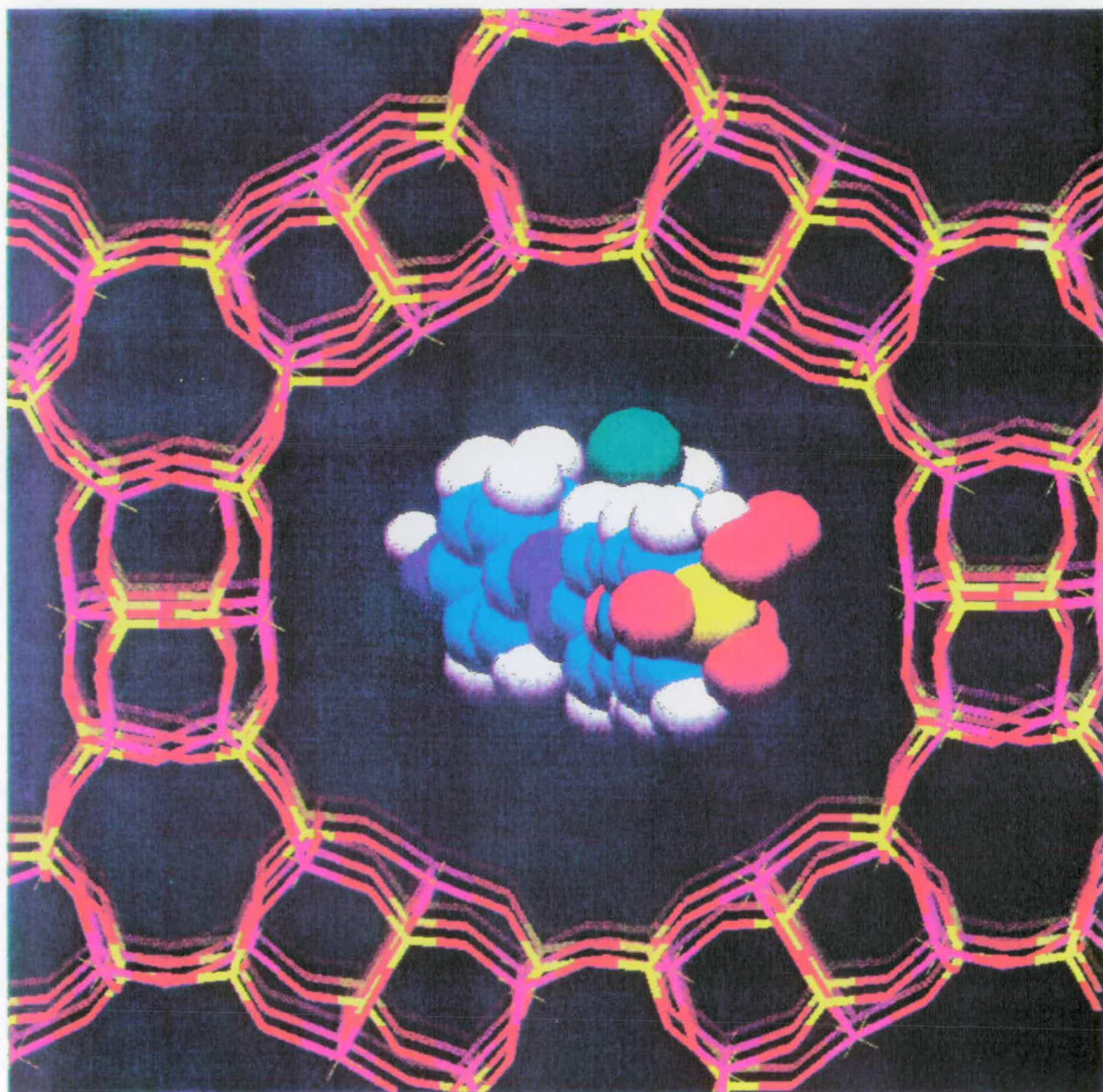
In summary the properties of zeolites dependent upon Si / Al ratio are ion exchange, water sorption, and catalytic activity

1.4.2 Uses

Most 'traditional uses' of molecular sieves are confined to zeolites, this is not only because they have been known for longer, but also because many of the uses rely on the properties engendered by their charged frameworks. The traditional uses include ion-exchange, catalysis and sorption (including desiccation and gas separation / purification) [47]. Examples of each of these are:

- Zeolite ion exchangers are used in applications as diverse as phosphate replacement in washing powders, soil conditioning, and effluent treatment in the nuclear reprocessing industry.
- The major use of hydrogen-exchanged zeolite Y is as a hydrocracking catalyst in the oil industry for the production of petrol from heavier fractions. Its introduction in 1964 actually led to a drop in cracking capacity in the USA because it gave such improved yields of the desired fractions than the amorphous silica-alumina catalysts which had preceded it [48].
- Zeolites are used as potent scavengers of water to dry gases and organic liquids [3]. They are used in important industrial separations such as the separation of branched from linear hydrocarbons or the separation of oxygen from air. Although sorption by molecular sieves is dominated by zeolites, especially since much relies on the charged frameworks, it is in this area that other molecular sieves have the most potential, particularly those such as VPI-5 which have extra-large pores not found in zeolites. As an example Figure 1.7 shows how easily a large organic molecule fits into a VPI-5 channel. The same molecule is too large to fit into zeolite Y.

Figure 1.7 A large organic molecule (kinetic diameter approximately 9Å) fits easily into VPI-5



Much current research has focused on finding new uses for molecular sieves, which are based on filled materials where the molecular sieves have materials loaded into them so as to achieve novel or enhanced properties from the sorbate. Many of the ideas are for applications in the field of electronics and are outlined in a review by Ozin *et al* [49]. Amongst the ideas being investigated are the construction of discreet clusters (nanoclusters) of materials within zeolites and the construction of 'molecular wires'.

The confinement of discreet clusters of semiconductors inside the pores of zeolite hosts has profound effects on the semiconductor optical properties and several uses for this are being looked at. The clusters may be catalysts for photoinduced electron transfer reactions in which case the use of zeolites adds chemical selectivity to the reactions [50]. A more high-tech vision is that the low dimension of the clusters (so-called quantum dots [49]) will make electron excitation or transfer processes faster and more energy selective which will enable them to act as extremely fast switches for optical or opto-electronic devices, e.g. lasers, switches and electronic data storage systems [51,52,53]. Further work, on nanocomposites of silver salts within zeolites, promises high density data storage systems or high resolution imaging / printing materials [54]. Attempts to create 'molecular wires' involve the synthesis of strands of conducting polymer such as polypyrrole or polyacrylonitrile in the channels of zeolites [55,56]. If successful this could lead to ultra-miniaturisation of electronic circuitry. Between them the semiconducting particles and the molecular wires could form the basis of nanometre-scale electronics.

Another set of filled materials which are being investigated for their potential use as data storage devices are dye-loaded molecular sieves [51,57]. It is claimed that molecular sieves make good hosts for dyes such as methylene blue which is a suitable candidate for optical data storage through persistent spectral hole burning [58]. Molecular sieves filled with another coloured organic, para-nitroaniline (PNA) have also been reported to show novel optical properties [59]. They exhibited anisotropic light absorption due to the orientation of the molecules of PNA in the channels of ZSM-5, AlPO_4 -5, and VPI-5. A potential use for such materials is as polarisers.

1.5 Aims of this Work

In this work the aim was to study the uptake of dyes into molecular sieves, with particular emphasis placed on VPI-5 due to its extra-large pores. In order to be able to use VPI-5 for that purpose it was first necessary to make a thorough investigation of its synthesis and thermal stability.

Chapter 3 describes the synthesis of VPI-5. It details a systematic investigation of two different synthesis routes, undertaken in order to determine the conditions from which each route would produce a high purity product. The chapter describes the adaptation of one of these routes, a clear solution synthesis, to enable the study of the growth of large single crystals of VPI-5. Evidence is presented which sheds more light on the debate about the similarities between VPI-5 and the aluminophosphate H1.

Chapter 4 investigates the thermal stability of VPI-5. The factors which most affect the thermal transformation of VPI-5 to $\text{AlPO}_4\text{-8}$ are elucidated and methods are determined by which the structure may be made more stable. The activation energy for the transformation of a particular batch of VPI-5 to $\text{AlPO}_4\text{-8}$ is calculated.

Chapter 5 systematically investigates the best route and optimum conditions for maximum dye uptake into VPI-5. High loadings, of up to 4% w/w, are achieved for several dyes. It is shown that sorbed organics can enhance the thermal stability of VPI-5. It is also shown that the stability to UV irradiation of a dye trapped within VPI-5 is improved.

Chapter 6 describes experiments designed to load zeolites X, Y and ZSM-5 with dyes. The routes which are investigated involve sorption or uptake from synthesis gel. There is successful uptake of dyes into zeolites X and Y, especially dealuminated zeolite Y. This shows the effect of framework aluminium content on the sorption of organics. Colour changes are seen when dealuminated zeolite Y, loaded with waxoline yellow RPFW, is dehydrated.

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Chapter 2

Materials and Techniques

This chapter outlines the chemicals and reaction vessels used for the experimental parts of this study, and the analytical methods used to examine the products. Details of particular experimental techniques employed are described in the relevant chapters.

2.1 Materials

2.1.1 Chemicals

The chemicals used throughout the work are listed below:

Zeolite X (BDH, Lab Reagent)

Zeolite Y (Strem)

Dealuminated Zeolite Y

Phosphoric Acid (BDH, AnalaR, 85%)

Pseudoboehmite (Kaiser Alumina, 30% H₂O w/w)

Catapal A (Vista)

Catapal B (Vista)

Di-n-propylamine (Aldrich, 99%)

Triisopropanolamine (TiPOA) (Aldrich, 95%)

Tetramethylammonium hydroxide (25% soln in H₂O), (BDH, Lab Reagent)

AlCl₃ (anhydrous) (BDH, AnalaR)

Polyethylene Glycol 6000 (BDH, Lab Reagent)

Waxoline Blue APFW (ICI)

Waxoline Orange EPFW (ICI)

Waxoline Orange 3GPFW (ICI)

Waxoline Red O (ICI)

Waxoline Yellow 2GPFW (ICI)

Waxoline Yellow 3GPFW (ICI)

Dispersol Yellow C-5GN (ICI)

H113471 (ICI)

H104479 (ICI)

Polyethylene (Spectroscopy grade, BDH)

Azulene (Aldrich)

15-Crown-5 (Aldrich)

Quinaldine Blue (Aldrich)

N,N-Dimethylindoaniline (Aldrich)

Distilled water

2.1.2 Synthesis Vessels

In order to meet various different criteria, a range of vessels was used for the synthesis of molecular sieves in this study. They ranged from large vessels, designed to produce large amounts of material from known recipes, to small vessels used once only for the investigation of novel syntheses. Listed below are the vessels which were used:

Soda-glass Melting Point Tubes

These standard 10cm long melting point tubes were used for a range of experiments in the MFI and APHE systems. They enabled a large number of reactions to be carried out simultaneously due to the small amount of reactants required per tube and the small amount of space occupied by each tube. This enabled a range of crystallisation times and temperatures to be studied in a short time for a given reaction composition.

All reaction mixtures were aqueous solutions or suspensions and this usually enabled tubes to be filled by capillary action. Each tube was dipped into the reaction mixture and allowed to take up about 3cm of solution (approx. 0.04cm^3). This had been found by Franklin [1] to be an optimum amount of mixture; enough solid material was produced for X-ray analysis, if crystallisation was successful, whilst internal pressure in the tube was unlikely to become high enough to burst the tube. In some cases the reaction mixture was too viscous for capillary action to work and a syringe and needle were used.

Once filled, the tube ends were wiped clean, the reaction mixture was centred and the ends of the tubes were sealed. The dry end was sealed first, by rotation in a micro-burner flame. This method could not be used on the end through which reaction

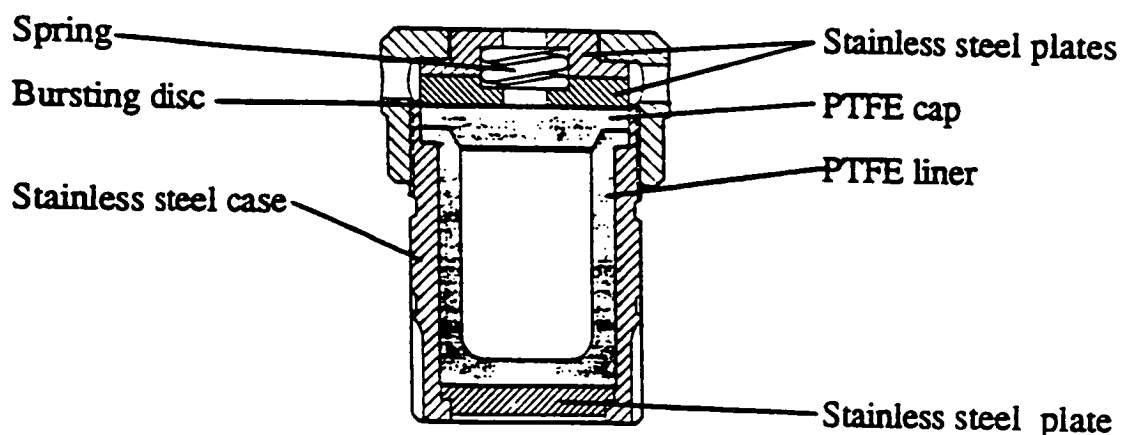
mixture had been drawn as heat would often cause residual reaction mixture on the inside of the tube to form a deposit as solvent evaporated. The deposit prevented the glass from melting together to form a perfect seal. To overcome this problem, these ends were sealed by drawing out the glass in a flame, which provided a clean glass surface for seal formation.

Sealed tubes were heated in preheated precision ovens, in drilled out aluminium blocks which allowed the tubes to lie horizontally. Tube contents could be examined under an optical microscope whilst the tubes were sealed. In some experiments tubes were taken from the oven to the microscope in the hot aluminium block and examined very quickly under the microscope. This kept the contents of the tube hot, thus, if crystallisation had not occurred, the tubes could be placed back in their oven with only a slight interruption to synthesis.

PTFE Lined Vessels

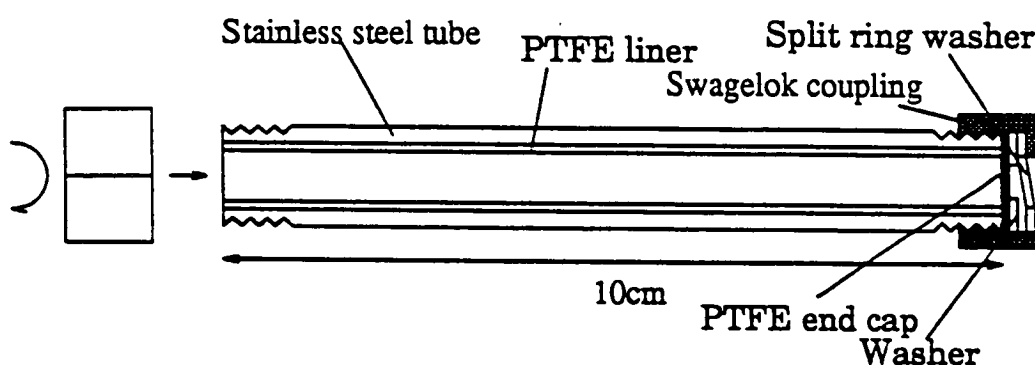
Parr Bombs. These are commercially available pressure vessels (Parr, Illinois), which consist of a PTFE liner in a stainless steel case (Figure 2.1). The steel lids have a hole in the top and between the hole and the lid of the PTFE liner there is a bursting disc - a thin sheet of metal. If the pressure inside the bomb gets dangerously high, safe release occurs by means of the PTFE lid piercing the disc and releasing pressure through the hole in the steel lid. Two sizes of bomb were used in this work, 23ml (type 4749) and 125ml (type 4748). Both types were normally filled with synthesis mixture to about 60% capacity. They were heated, without stirring, in preheated ovens.

Figure 2.1 Parr bomb



Tube Bombs. These are small reaction vessels, made of stainless steel with PTFE liners, which were developed by K.C.Franklin in Edinburgh [1], their name is often abbreviated to TOMS. The design of a TOM is shown below (Figure 2.2). With a capacity of 3ml, TOMS were able to play a similar role to glass tubes, in that a large number of times and temperatures could be studied for a given reaction mixture without the use of too much material. Their advantage was that the reaction was carried out in a PTFE liner, which was new each time to eliminate any unwanted seeding effects. The liner consisted of a 10cm tube of PTFE ($\frac{1}{4}$ inch I.D., $\frac{5}{16}$ inch O.D.), cut carefully so that the ends were square, and two end-caps stamped from a 2mm thick sheet of PTFE. Tightening the nuts at either end of the TOMS was sufficient to enable the caps to provide a satisfactory seal. As with the other synthesis vessels, filled TOMS were placed into preheated ovens for synthesis reactions.

Figure 2.2 Tube bomb

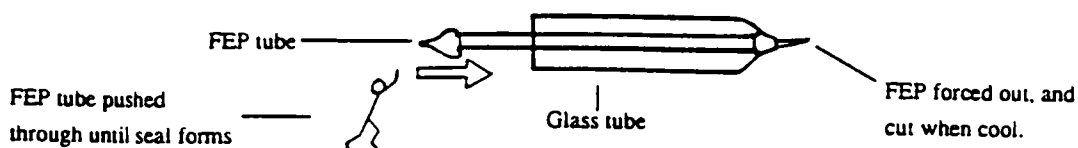


FEP Tubing. There was a requirement for vessels which allowed controlled dehydration to be carried out. Fluoroethylene polymer (FEP) tubing was found to be an ideal material to make these vessels from: It was unreactive, easy to seal, could be used at high temperatures, and became slightly permeable to water when hot.

The method by which the vessels were made was to cut standard 10cm lengths, these were then sealed at one end. A known weight of the sample to be dehydrated was put into the tube, using a long-stemmed glass funnel so that no sample adhered to the open end of the tubing. The open end was then melt sealed also and the vessel heated in an oven to facilitate dehydration. Figure 2.3 shows how a hot glass tube, tapered at

one end, was used to seal the FEP tubing. The dimensions of the FEP tubing were $\frac{1}{4}$ inch I.D., $\frac{5}{16}$ inch O.D.

Figure 2.3 Method of sealing FEP tubes



2.1.3 Ovens

Work was carried out at temperatures which ranged from 65 to 950°C. Most work below 150°C was done in Perkin Elmer precision ovens, from old PE F11 gas chromatographs, although some synthesis reactions used a Gallenkamp oven (300 plus series). In descriptions of synthesis work it is stated which oven was used. For temperatures above 150°C a Gallenkamp box oven (size 1) was used.

2.2 Analytical Techniques

A range of analyses were required:

- The structures of synthesis products had to be examined to see whether they were the desired material, and of sufficient purity.
- Due to its thermal instability samples of VPI-5 had to be examined for signs of $\text{AlPO}_4\text{-8}$ formation if they had been heated.
- For dye-loaded materials changes to the spectra of the dye were to be looked for and thermal analysis gave clues as to whether or not dye was sorbed.

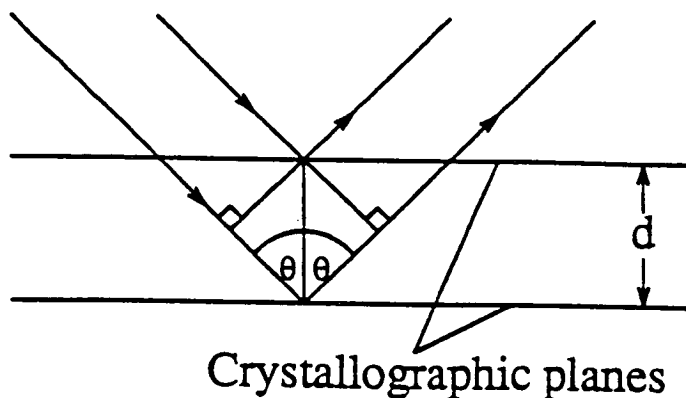
Brief accounts of the treatments used to examine the samples are given below.

2.2.1 X-ray Powder Diffraction

X-ray powder diffraction (XRPD) is a widely used technique for the identification of crystalline molecular sieves. Each material generates a unique X-ray diffraction pattern based on the arrangement of atoms within the crystals. XRPD can be used to provide detailed structural information, especially in the light of recent advances such as the use of synchrotron radiation and Rietveld refinement, however in this work XRPD has primarily been used as a fingerprint technique for the identification of known materials, rather than for structure determination. By careful analysis of diffraction patterns and the use of standards it is also possible to use XRPD to calculate the relative amounts of two different phases occurring in the sample.

A beam of X-rays directed at a crystalline material is diffracted (Figure 2.4) because the wavelength of X-radiation is of the same order of magnitude as the interatomic distances found in crystalline materials.

Figure 2.4 X-ray diffraction



θ = angle of incidence of the X-ray

λ = wavelength of the radiation

This process is described mathematically by the Bragg equation:

$$n\lambda = 2d\sin\theta$$

where n = a positive integer

d = distance between crystallographic planes

θ = angle of incidence of the X-ray

λ = wavelength of the X-radiation

The diffraction patterns produced are plots of intensity against diffraction angle, 2θ . Powder diffraction requires the sample to be ground to a fine powder so that a large number of particles are analysed. In most systems this leads to random orientation of the crystallites and thus the Bragg condition for reflection to take place from every possible interplanar spacing is fulfilled. A problem which can occur, especially with needle or plate-like morphologies, is preferred orientation in which, as the name suggests, there is no longer a random orientation of the crystallites. This changes the relative intensities of peaks in the diffraction pattern and can make analysis of data more difficult.

XRPD was carried out using a Phillips Powder Diffractometer. Cu-K α X-rays of wavelength 1.5418Å were generated by a PW 1730/10 stabilised X-ray generator. Mounted on top of this were a PW 1050/70 goniometer and PW 1965/60 proportional detector whose output was recorded on a chart recorder. If there were large quantities of material the samples were packed into rectangular sample holders, pressed flat and analysed. More usually, due to the small amounts of material used in most of the experiments in this project, samples were sprinkled onto specially cut wafers of silicon single crystal, upon which they were held in place by a thin layer of silicone grease. The use of silicon wafers increased the problem of preferred orientation effects.

Unless otherwise stated, the running conditions were as follows:

Tube voltage	40kV
Tube Current	30mA
Scan Angles	30 to 3°2 θ
Range	2 x 10 ³ counts s ⁻¹
Step angle	1° 2 θ min ⁻¹

XRPD was used to identify synthesis products and to examine samples of VPI-5 or signs of $\text{AlPO}_4\text{-8}$ formation. This was straightforward and involved recording XRPD patterns of samples after attempts to load them with VPI-5 and also after any subsequent treatments. What was looked for were signs of $\text{AlPO}_4\text{-8}$ formation as this would indicate that conditions had been too harsh. Once $\text{AlPO}_4\text{-8}$ had formed then it would be unlikely that any more dye would be able to enter the channels and also unlikely that any sorbed dye would be able to escape.

2.2.2 Thermal analysis

Thermal analysis techniques measure the change in a property of a sample as it is heated. Three types of analysis were employed, thermogravimetric analysis, differential thermal analysis, and differential thermal gravimetry. Samples are heated linearly from ambient to temperatures as high as 1673K, but more typically 1173K. The rate of temperature increase varies from 1 to 10Kmin^{-1} , usually 10K. Between them, the techniques can provide information on the temperatures at which water or organics are lost from a molecular sieve and also how much of each type of substance was present. Most samples are examined under flowing air, however an inert atmosphere, e.g. Nitrogen, or static air can also be used.

Thermogravimetric Analysis (TGA)

In this method of analysis the mass of a sample is continuously recorded as the sample is heated. The resultant thermogram shows the weight lost and can also give a qualitative estimate of the temperature at which the loss occurred.

Differential Thermal Analysis (DTA)

By measurement of the temperature difference between the sample and a reference (usually of alumina), which are heated at the same rate, DTA records exothermic and endothermic events. This information can be useful for giving clues as to whether an organic has been sorbed into a molecular sieve framework. A typical DTA for an organic containing molecular sieve shows an endotherm between 373 and 473K which corresponds to dehydration, and a series of exotherms between 523 and 923K which correspond to the combustion of organic located in different areas of the framework.

Differential Thermal Gravimetry (DTG)

This is the differential of the TGA weight loss curve and records the rate of change of weight loss. The differential thermogram is recorded as a series of peaks rather than

steps and may reveal information which is not detectable in the ordinary thermogram, such as a point of inflection on what looks like a single step on the TGA thermogram. This would indicate that there were two steps instead of one.

TGA was carried out on a Stanton Redcroft TG770 instrument, DTA on a Stanton Redcroft DTA 673-4, and combined TGA, DTA, and DTG on a Stanton Redcroft STA-780 simultaneous thermal analyser. Data from the STA-780 was collected and processed on a BBC microcomputer.

2.2.3 Optical Microscopy

For much of the synthesis work in this project optical microscopy was the first or only analytical technique used to characterise the products. A Vickers M41 Photoplan microscope was used, fitted with a splitter and 35mm camera. Reaction products were identified by their morphology.

The advantage of optical microscopy over the more accurate technique of XRPD is that it is very quick, especially in work, such as some that will be described, where the desired products have very distinctive morphologies. This enabled a series of samples to be removed in quick succession once crystallisation was seen to start, which helped to improve the efficiency of time dependent studies where the product appeared in only a narrow window of time. It was especially useful when the window of time was which was shorter than the time it would take to run an XRPD. The other benefit of the optical microscope was that it enabled samples to be screened for large single crystals of VPI-5 (Chapter 3). Although the crystals that were sought were deemed large (10 x 250µm), they were still too small to find with the naked eye or a hand lens.

2.2.4 Scanning Electron Microscopy

Scanning electron microscopy (SEM) produces images of higher magnification and greater depth of field than optical microscopy. For these reasons it was useful as a means of acquiring detailed information on crystal morphology and crystal aggregates.

Prepared samples are placed in a vacuum chamber and scanned by a fine, high energy electron beam in a series of parallel lines known as a raster. The incident electrons cause the atoms in the sample to emit low energy secondary electrons. These are collected in a suitable detector, the number of electrons emitted being a function of the physical nature of the surface and its angle to the incident beam. Also detected are some of the high energy beam electrons which are reflected from the surface. The

detector signal is amplified and displayed line by line on a cathode ray tube (CRT) which scans synchronously with the incident beam. SEM does not use lenses, instead magnification is a function of the dimensions of the scanned region. Resolution can be increased by narrowing the electron beam and increasing the acceleration voltage. A second, ultra-high resolution CRT allows photographic recordings of images (electron micrographs).

Samples were prepared for SEM analysis by dispersion upon an Aluminium stub with acetone. Once the acetone had evaporated, the samples were coated with Gold in an Argon atmosphere. The Gold coating serves two purposes, firstly it improves the clarity of the image since the number of secondary electrons emitted is directly proportional to atomic number and so the electron emission is greatly increased. Secondly the Gold coating helps to earth current from the sample. This is important since a build up of electrons on the sample surface can lead to gross image distortion and sample damage.

A Cambridge Instruments Stereoscan 250 scanning electron microscope located in the Science and Engineering faculty SEM unit was used to produce the micrographs used in this work. Gold coating, film processing and instrument calibration were done by Mr J.Findlay.

2.2.5 UV/visible spectroscopy

With the use of dyes in this work a feature which was immediately looked for was change in the colour of free and sorbed dyes. Many interactions can affect the actual or apparent colour of dye, the most likely one to occur to a dye sorbed inside an aluminophosphate molecular sieve is related to lack of space. In this case the interaction could act to restrict the free rotation of some part of the molecule involved in the electronic transitions giving rise to bands, thereby altering the colour [2].

The physical form of coloured particles can also affect the apparent colour. This is due to changes in the nature of the light reflected from them. Thus one might expect to see differences in the colours of a very fine powdered dye and coarse crystals of molecular sieve which contain the same dye. For this reason much effort was devoted to the development of a method whereby samples could be analysed by UV/visible spectroscopy. In the absence of a reflectance UV/visible spectrophotometer efforts were made to devise a technique by which the powders of dye and molecular sieve could be successfully analysed by an absorption method.

The problem with UV/vis spectroscopy was that it is usually done on solutions, whilst in this work the investigation needed to be carried out upon solids. Several workers have reported the analysis of solids by absorption spectroscopy. Pollack *et al* [3] looked at colour formation in styrene-zeolite complexes by mixing samples with Nujol and sandwiching the mulls between glass plates. Unfortunately this technique was not appropriate here since the dyes to be used were readily soluble in Nujol and so leaching of dye from complexes could lead to incorrect spectra.

The technique which was used was one which was first reported in 1952 by Stimson and O'Donnell [4]. They found that with careful preparation it was possible to use KBr discs to look at the UV spectra of solid organic compounds. The work was taken further by Wyman [5], who looked at the UV/visible spectra of insoluble dyes and pigments, and by Timmons [6] who defined the lower limit of the technique as being at 240nm, at which point transmission through a good KBr disc fell to 15%. It was also stated by Timmons that the technique could tolerate small amounts of impurities, including water, an advantage where hydrophilic molecular sieves were to be used.

The method used to collect absorption spectra of powders was to mix approximately 1mg of dye or 5mg of dye/VPI-5 with 150mg KBr. The substances were thoroughly ground together and pressed in a 13mm die for 30 seconds under 10 tonnes. Spectra were recorded on a Perkin-Elmer Lambda 9, a Perkin Elmer 402, or a Pye Unicam SP8-400, with KBr reference discs. By this method many spectra were collected of free dyes, dyes mixed with inert alumina, and dye/VPI-5 complexes.

Some work was also done on trying to collect spectra from polythene discs. These were made with spectroscopy grade polythene (BDH) which it was hoped would be more optically transparent than KBr. Unfortunately it proved to be difficult to produce polythene discs of good quality.

Attempts were also made to collect diffuse reflectance UV/visible spectra, both from powders and also from samples of dye or dye/VPI-5 complex which were coated onto plastic films by means of a resin binder. The method was tricky and did not produce better spectra than KBr discs, therefore it was not developed further.

2.2.6 Infra Red Spectroscopy

Containment of organics within microporous materials can influence their modes of molecular motion [7]. This manifests itself in a variety of ways which can include alteration of the vibrational frequencies. In order to look at the vibrational properties of free and occluded dye IR spectroscopy was used.

A Perkin Elmer 577 and a Bio Rad FTS-7 infra-red spectrophotometer were used to collect transmission spectra from samples pressed into discs with KBr. Attenuated total reflection IR spectra were recorded with the Bio Rad FTS-7 spectrophotometer fitted with a Spectra Tech KRS-5 prism. Samples for ATR were in the form of melinex films coated with sample. Spectra of powders (dye, molecular sieve, or a mixture of the two) were collected by diffuse reflectance infra-red spectroscopy (DRIFTS), again on the Bio Rad FTS-7, with a Spectra Tech DRIFTS attachment fitted.

2.2.7 Raman spectroscopy

It was intended to use laser Raman spectroscopy as a method of looking at dyes within VPI-5, which was largely unaffected by the aluminophosphate framework. The hope was that the route could be used to measure dye uptake and identify interactions between dyes and VPI-5. Work was carried out at ICI Wilton, with spectra collected by Dr N. Everall and Dr J. Lumsdon.

Trials showed that a conventional Raman system (Dilor XY Raman spectrometer, using the 514nm line from a Spectra-Physics 2035 argon ion laser) caused the VPI-5 framework to fluoresce to such a high degree that satisfactory spectra could not be obtained. It is thought that transition metal impurities were the actual cause of the fluorescence as the framework should not intrinsically have been fluorescent.

The fluorescence meant that Raman work had to be carried out with infra-red on a Perkin-Elmer 1700X Fourier transform Raman spectrometer, equipped with a 1.06 μ m Nd:YAG laser. Backscattering spectra were collected with an InGaAs detector. This equipment had its problems also, some dyes fluoresced very badly so that no Raman spectra could be collected from samples which contained them. This limited the scope of Raman spectroscopy in this project.

2.2.8 Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) spectroscopy involves the orientation of nuclei with respect to an applied magnetic field and their irradiation with a radio frequency to induce transitions among allowed energy levels. In this process radiation is absorbed, which gives information on the structure of materials.

The theory behind NMR involves the assumption that nuclei rotate about an axis, that is they have nuclear spin. Since nuclei are charged, the spin will generate a magnetic field, which results in a magnetic dipole oriented along the axis of spin. Nuclei have discrete spin states, the number of which is related to the nuclear spin quantum number, I , such that there are $2I+1$ spin states. In the simplest case for which NMR is possible $I=1/2$, thus there are two possible spin states.

Normally the two states are degenerate, but if the nucleus is exposed to an external magnetic field they split. This is because the magnetic moment, and hence the spin axis, aligns parallel to the field, either with or against it. The spin axis aligned with the field has a lower energy than that which is aligned against the field and so the two energy levels have different populations, their ratios determined by the Boltzmann equation.

The difference in energy between the different spin states is very small and the appropriate energies lie in the radio-frequency part of the spectrum. Irradiation of nuclei by the appropriate energy can cause them to undergo transitions from the aligned to the opposed orientations and vice versa. This resonance leads to a net absorption since there are more nuclei in the low energy state than in the high energy state. A plot of absorption of radio-frequency against frequency produces an NMR spectrum.

The chemical environment of an atom affects its resonance frequency by a few parts per million. This is known as chemical shift and is normally expressed as the difference in frequency from some given standard, e.g. phosphoric acid (H_3PO_4) for ^{31}P . Chemical shift can be correlated with molecular structure and it is this for which NMR is most used. If the magnitude of the external magnetic field is increased then the resonance frequencies for nuclei increase. Since chemical shifts are fractions of the resonance frequency rather than absolute values, they too get larger and so better spectral resolution is possible. The references contain more detailed descriptions of the theory of NMR.

In this study, solution and solid state ^{31}P , and solid state ^{27}Al NMR were carried out. There are large differences between solution and solid state NMR which arise from the way in which nuclei interact in the different states. In solutions, only interactions with nuclei in the same molecule are important, as interactions with other molecules are averaged out to zero due to their rapid and isotropic motion. Thus solution NMR spectra can more or less be collected in the simple fashion described above.

When solids are studied, the collection of meaningful data becomes more complicated. No longer is intermolecular shielding averaged out to zero, there are strong anisotropic effects upon shielding, this is chemical shift anisotropy. Theory shows that anisotropic shielding falls to zero when molecules are orientated at an angle of 54.7° to the applied magnetic field and so that is what is done, with the samples being spun at the same time, so that the technique is known as Magic Angle Spinning NMR.

MASNMR was carried out on Aluminophosphates by Dr N.J.Clayden at ICI Wilton, using a Bruker MSL200 NMR for ^{31}P and a JEOL GX-400 NMR for ^{27}Al . Previous studies on AlPO_4s have shown NMR to be a very useful tool for their analysis. Solution ^{31}P NMR was done at Edinburgh on a JEOL FX90Q NMR with the help of Mr S.Black.

Further information on NMR can be found in the many text books on the subject, e.g. [8,9].

2.2.9 Analysis of Thermal Stability

Analysis of the thermal stability of VPI-5 played an important part in this work. Therefore a variety of methods were used to heat VPI-5 so that its thermal stability might be investigated. Investigations were carried out on both as-made VPI-5 and on VPI-5 which had been loaded with dyes. It was thought, and there had been evidence from other workers [10,11], that the presence of large organic molecules within the pores of VPI-5 might enhance its thermal stability. The idea was that the organics could act as structural scaffolding which was too bulky to allow the contraction of VPI-5 to $\text{AlPO}_4\text{-8}$.

The general method for investigating thermal stability was to heat samples in air. A range of temperatures were used but it was generally one or all of:

a) 80°C for varying lengths of time - this relatively low temperature slowly dehydrated VPI-5 and was found to be very good for inducing $\text{AlPO}_4\text{-8}$ formation.

Samples of 10-15mg were spread thinly on the base of glass vials and put into a preheated oven.

b) 750°C - small amounts of sample were placed in the bottom of platinum crucibles, heated to 750°C from room temperature at a rate of approximately 15°C min⁻¹, and held at 750°C for 30 minutes. The hot crucibles were removed and left to cool in ambient air. The atmosphere in the furnace (static ambient air), the heating rate, and the final temperature represented the worst possible conditions that samples were likely to face if put in for micromeritics pore volume measurement.

c) 950°C - samples heated from room temperature at 10°C min⁻¹ in flowing dry air. These were samples which had undergone thermal analysis. The residues were examined by XRPD to find out how the VPI-5 structure had coped with these conditions..

Methods b and c will be referred to solely as 750 and 950°C in later Chapters.

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Chapter 3

Synthesis of VPI-5

3.1 Introduction

VPI-5 is not available commercially and so it had to be synthesised in Edinburgh. The synthesis process itself became an area of study in order to compare which materials and conditions would produce the best product with which to carry out other research. As well as the synthesis of VPI-5, a small amount of work was done on the synthesis of gallium phosphate molecular sieves from a precursor complex and on the synthesis of the zeolite ZSM-5 with dyes as templates. All of this work is described in the chapter which follows.

3.2 Synthesis of VPI-5 from Templated Gels

Templated gels are used for most molecular sieve synthesis and it was by such a route that Davis *et al* [1] first synthesised VPI-5. Their initial reports [1, 2] gave two different recipes from which VPI-5 could be obtained, each of which used a different organic template. n-Dipropylamine (DPA) was one of those templates and it was the template which was chosen for use in this work, due to ease of availability and low cost. Since then a number of other synthetic routes have been reported [3,4], most of which use organic-templated gels.

3.2.1 Synthesis of VPI-5

In this section work is described which sought to optimise the conditions by which VPI-5 could be synthesised from gels, initially templated with DPA after the work of Davis *et al* [1]. The synthesis procedure used for the initial synthesis was as follows:

1. Pseudoboehmite (9.57g, Kaiser Alumina) was slurried in distilled water (10.64g).
2. Distilled water (18.0g) was added to Phosphoric acid (15.16g, 85% H_3PO_4).

3. The phosphoric acid solution was added to the alumina slurry. The beaker which had held the phosphoric acid solution was washed out with water (10g) which was also added to the slurry.

4 The mixture was shaken for 1.75 hours at ambient conditions.

5. n-Dipropylamine (6.65g) was added to the mixture to form a gel.

6. The gel was aged, with shaking, for a further 1.5 hours at ambient conditions.

7. 60g of reaction mixture were put into a 105ml Parr bomb which was heated at 142°C for 23 hours in a Perkin Elmer PE111 gas chromatography precision oven.

Gel composition: DPA : Al_2O_3 : P_2O_5 : 40 H_2O (in terms of oxide ratios)

Although Davis *et al.* stated [2] that VPI-5 would start to crystallise from the above system within 5 hours, they suggested that a time of 20-24 hours gave the best crystallinity. Longer crystallisation times also acted as a buffer against any variation in the procedure, which tended to increase the crystallisation time.

The contents of the cooled vessel were slurried in water and the supernatant liquid was decanted. Water was added and decanted several times in order to wash the solids before they were filtered and dried in ambient air.

Initially synthesis of further batches of VPI-5 was only done when it was necessary to produce more for use as a starting material and conditions varied little from those used initially. However it was recognised that there were substantial quantities of impurity in the VPI-5 that was being produced. It had originally been thought that only trace quantities of impurity were present because XRPD patterns contained very small peaks which were attributable to impurity (see results, section 3.3.3 for quantification and explanation). Thus, syntheses were carried^{out} with the aim of improving the synthesis so as to produce as pure a sample as possible. The following variations were made to the reaction:

i) Reaction times were greatly shortened as it had been claimed by other authors [5, 6] that VPI-5 crystallised very rapidly and always before its impurities. Thus an increase in purity would offset the slightly lower crystallinity and yield caused by shorter reaction times.

ii) The synthesis temperature was lowered because it was claimed that $\text{AlPO}_4\text{-11}$ occurred only as a high temperature overrun product [2]. It was also thought that uneven heating may have played a part in $\text{AlPO}_4\text{-11}$ formation. Some synthesis was therefore carried out in a different oven, a Gallenkamp 300 plus. This was a much larger oven than the Perkin Elmer so that, although both oven types were forced convection, there should have been less chance of local areas of uneven heating in the Gallenkamp oven.

iii) Claims have been made [3, 7, 8] that more stable forms of VPI-5 can be synthesised by the use of different amines as templates. Attempts were made to synthesise superior stability VPI-5 by the use of Triisopropanolamine (TIPOA) and Tetramethylammonium Hydroxide (TMAOH) as templates [3]. The procedure was the same as before, except that the two named amines were added instead of DPA. The reaction composition was;



iv) A different alumina source (Catapal Alumina) was tried. Catapal B was the alumina source used by Davis *et al.* [1] and, although it has the pseudoboehmite structure just like Kaiser alumina, there have been claims [9, 10] that the different sources have different reactivities due to their micro-structures and that for some recipes only Catapal B will lead to the formation of VPI-5 [10]. Thus Catapal B was used in an attempt to synthesise purer, more stable forms of VPI-5, both from DPA-templated gels and from others. The syntheses from DPA templated gels were not expected to show improved stability, since even the use of Catapal B with DPA did not seem to have produced a very stable product [8, 11, 12], however the reactions were done for completeness sake. On the other hand the recipe chosen in part (iii) to try and produce more stable VPI-5 was one of those which was said [10] to work only when the alumina source was Catapal B.

3.2.2 Post-synthesis treatment of VPI-5

As has already been mentioned the VPI-5 made with DPA was washed, filtered and air dried. It was in this state that it was used initially, however various post-synthesis treatments were seen to improve the purity or stability of the VPI-5 and so these were carried out prior to use in later experiments. The treatments were as follows:

i) It was noticed early on that there were lumps of material present which were much harder than the majority of the sample, XRD analysis showed these hard lumps to be almost entirely composed of amorphous material. Most were very large and could be removed by sieving the dried product through a 30mesh sieve (500mm aperture size).

Further work looked at the effect of more extensive size gradation upon particle purity. Samples were put through 36, 60, 100, 150, and 200mesh sieves (approx. 400, 250, 150, 100, and 75 μ m aperture sizes) and XRPD patterns of the fractions were collected for analysis.

ii) Schmidt *et al* [13] stated that another phase was sometimes formed in VPI-5 synthesis, which consisted of very fine particles that slowly settled out of the slurry created when bomb contents were emptied. In order to try and get a purer product less time was allowed for material to settle before the supernatant liquid was decanted off. The supernatant liquid was centrifuged and solids collected, dried and examined by XRPD to see if this process really did lead to improved purity of product.

iii) The final post-synthesis treatment to be used was to contact VPI-5 with hot water. This did not seem to affect the purity of samples, but it was noted by several authors [8, 14] that the stability of VPI-5 could be improved if it was boiled in water: This was most probably due to removal of traces of organic impurity [14, 15]. Two related methods of stabilisation were tried.

Firstly samples of VPI-5 were placed in a round-bottomed flask which contained distilled water and had a condenser fitted. The water was heated to reflux for several hours.

The second method was a soxhlet extraction of VPI-5 with water, again for several hours. The effectiveness of the two methods were compared by experiments which tested the thermal stability of VPI-5.

These experiments are described in detail in chapter 4 along with discussion of the thermal stability of VPI-5.

3.2.3 Impurity Levels

Initially, levels of impurity in samples were assessed on a relative basis, but later it was possible to make up standard samples which contained known amounts of impurity. This allowed quantitative estimates of impurity content to be made. The change occurred when sufficiently pure samples of VPI-5, as well as of the phases commonly seen as impurities, had been produced. The sample of pure VPI-5 was obtained from reaction VS14a (see later, Fig. 3.9, for XRPD pattern) and was able to be used to make standards of known VPI-5 content. In addition samples of the impurity phases H3 and $\text{AlPO}_4\text{-11}$ were synthesised. H3 is a dense phase aluminophosphate, first identified by D'Yvoire [16]. Figure 3.1 shows the XRPD patterns of $\text{AlPO}_4\text{-11}$ and H3.

By careful addition of one of the impurity phases to VPI-5 in known ratios impurity standards made were for $\text{AlPO}_4\text{-11}$ and H3. Figures 3.2 and 3.3 show the XRPD patterns which were collected. The mixtures were analysed by XRPD and their peak heights and ratios measured. Strictly speaking it was the area of the peaks and not their heights which should have been measured, however all of the peaks were sharp and it was thought that any errors caused by measurement of heights would be balanced by errors to area measurement. These data enabled the impurity contents of VPI-5 samples to be measured more accurately than had been previously possible.

For each phase (VPI-5, H3, and $\text{AlPO}_4\text{-11}$) three lines were chosen to be used for calibration purposes, the lines occurred at $2\theta =$:

10.8, 18.8, and 27.2 for VPI-5

8.2, 15.7, and 20.5 for $\text{AlPO}_4\text{-11}$

12.8, 13.6, and 33.3 for H3

The chosen lines were relatively free from interference by lines from the other phases. They are marked for $\text{AlPO}_4\text{-11}$ and H3 in Figure 3.1 and for VPI-5 in Figure 3.6.

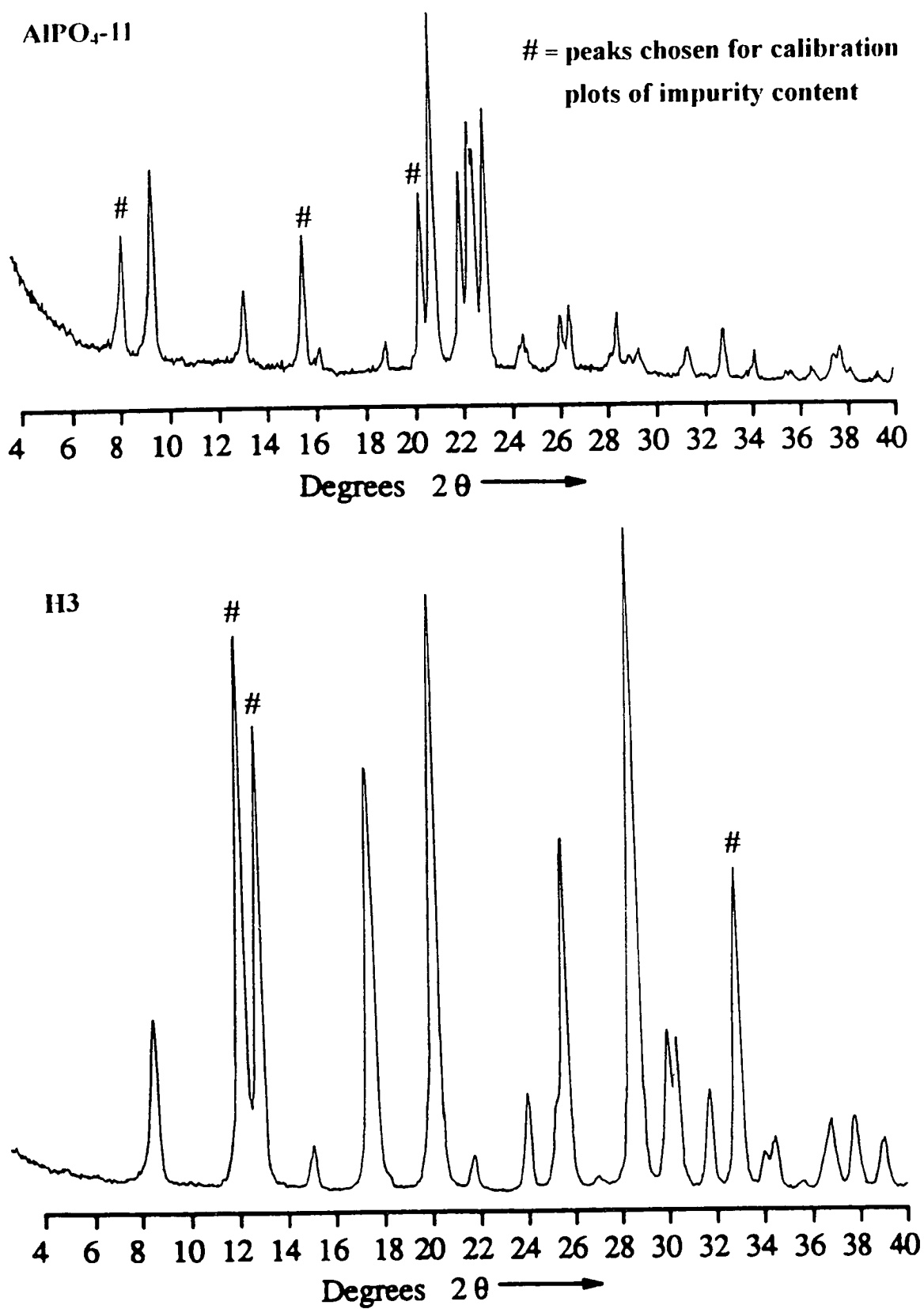
Figure 3.1 XRPD patterns of $\text{AlPO}_4\text{-11}$ and H3

Figure 3.2 XRPD patterns of standard mixtures of VPI-5 and $\text{AlPO}_4\text{-11}$

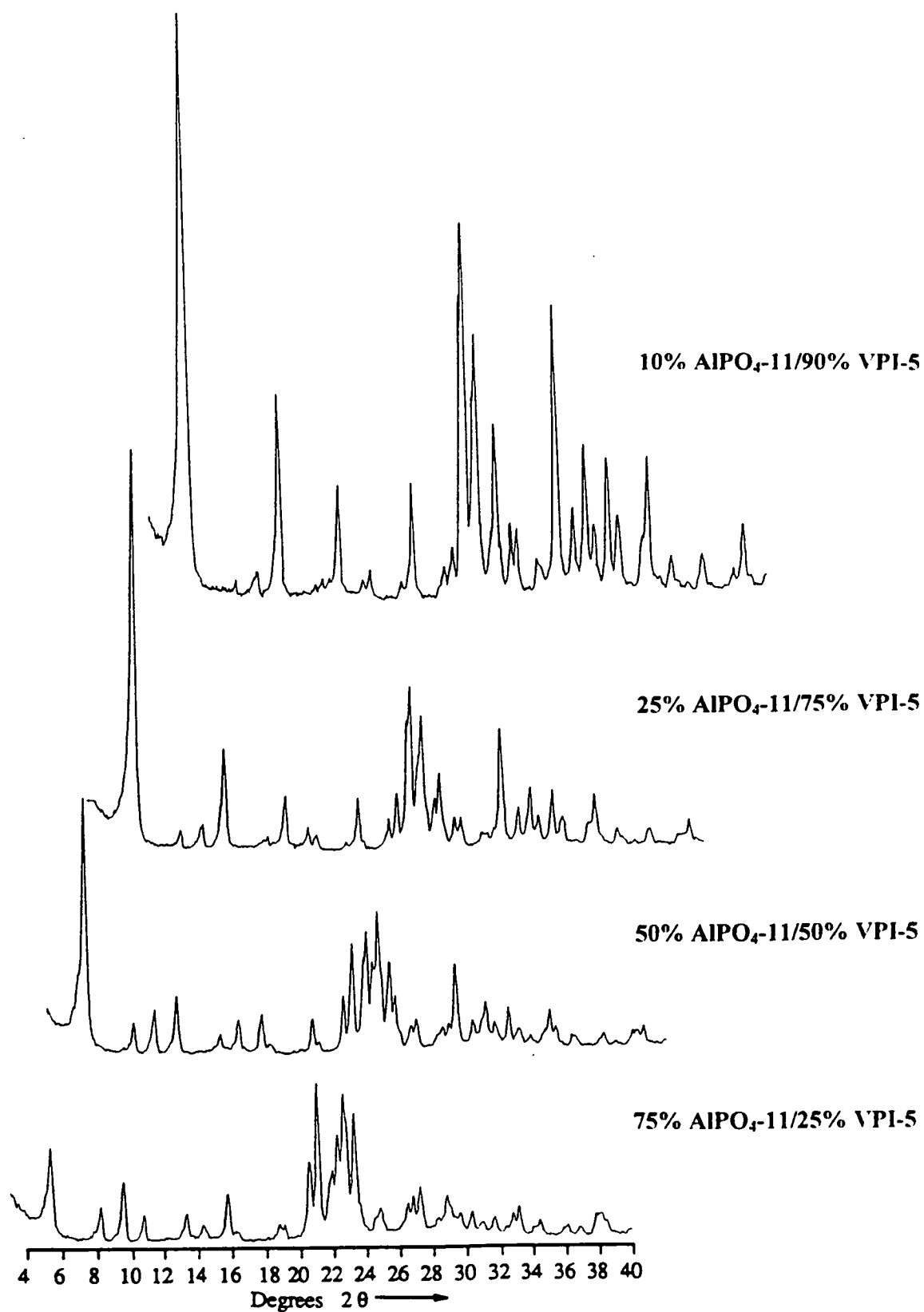
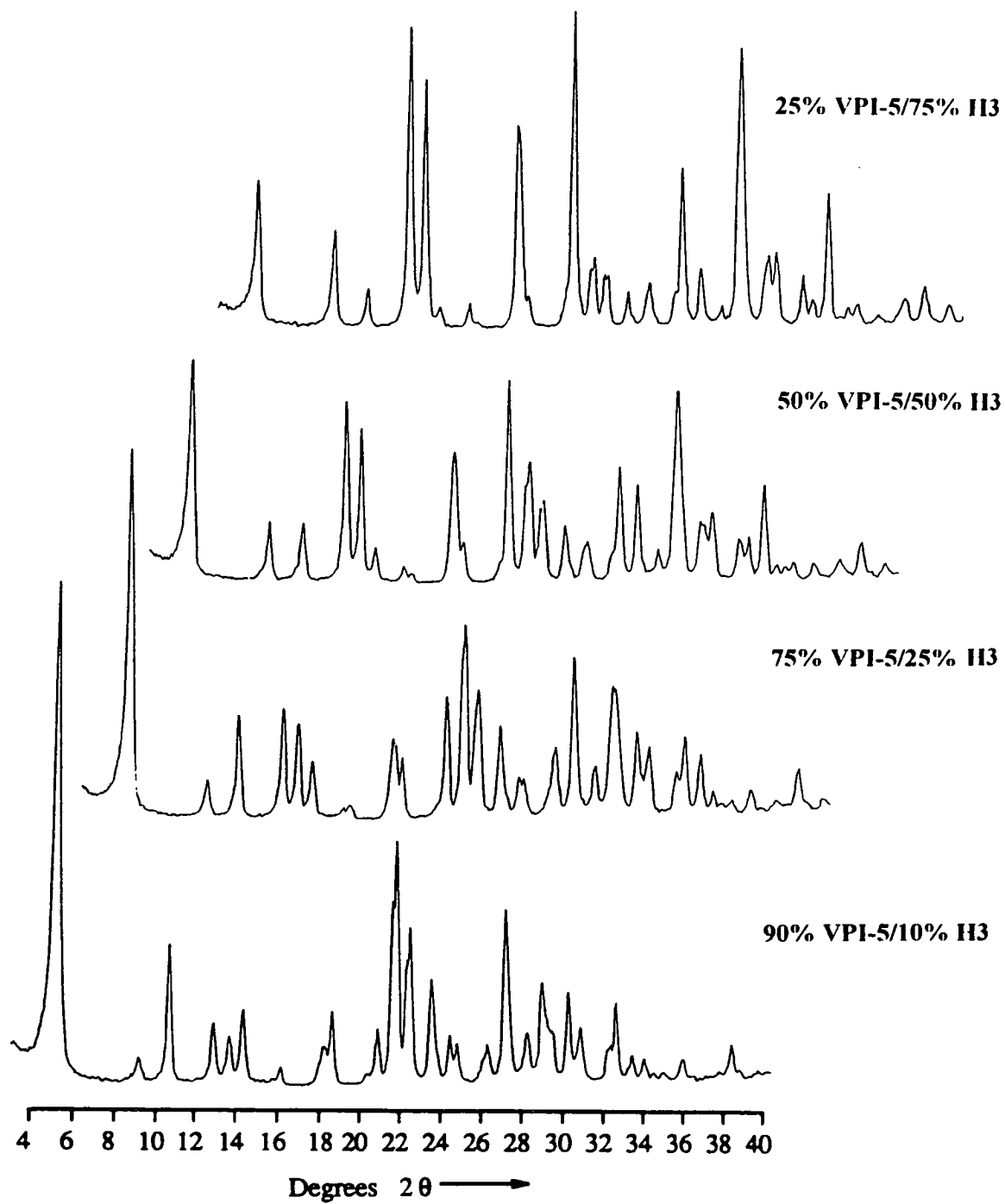


Figure 3.3 XRPD patterns of standard mixtures of VPI-5 and H3



In order to plot calibration curves the following procedure was used:

For each phase the heights of the chosen peaks were measured and summed.

The ratio was taken of the sum of the VPI-5 peak heights against the sum of the impurity phase peak heights for the given impurity.

Initially it was proposed to plot the ratio against impurity content and so obtain a calibration curve. However it was shown that when a plot of the natural log of the ratio was plotted against impurity content straight lines were obtained. These straight lines could then be used to obtain formulae from which estimates the impurity contents of samples could be calculated.

The calibration plots of impurity content vs. peak ratio are shown below in Figures 3.4 and 3.5.

Figure 3.4 Calibration plot of AlPO_4 -11 content in VPI-5

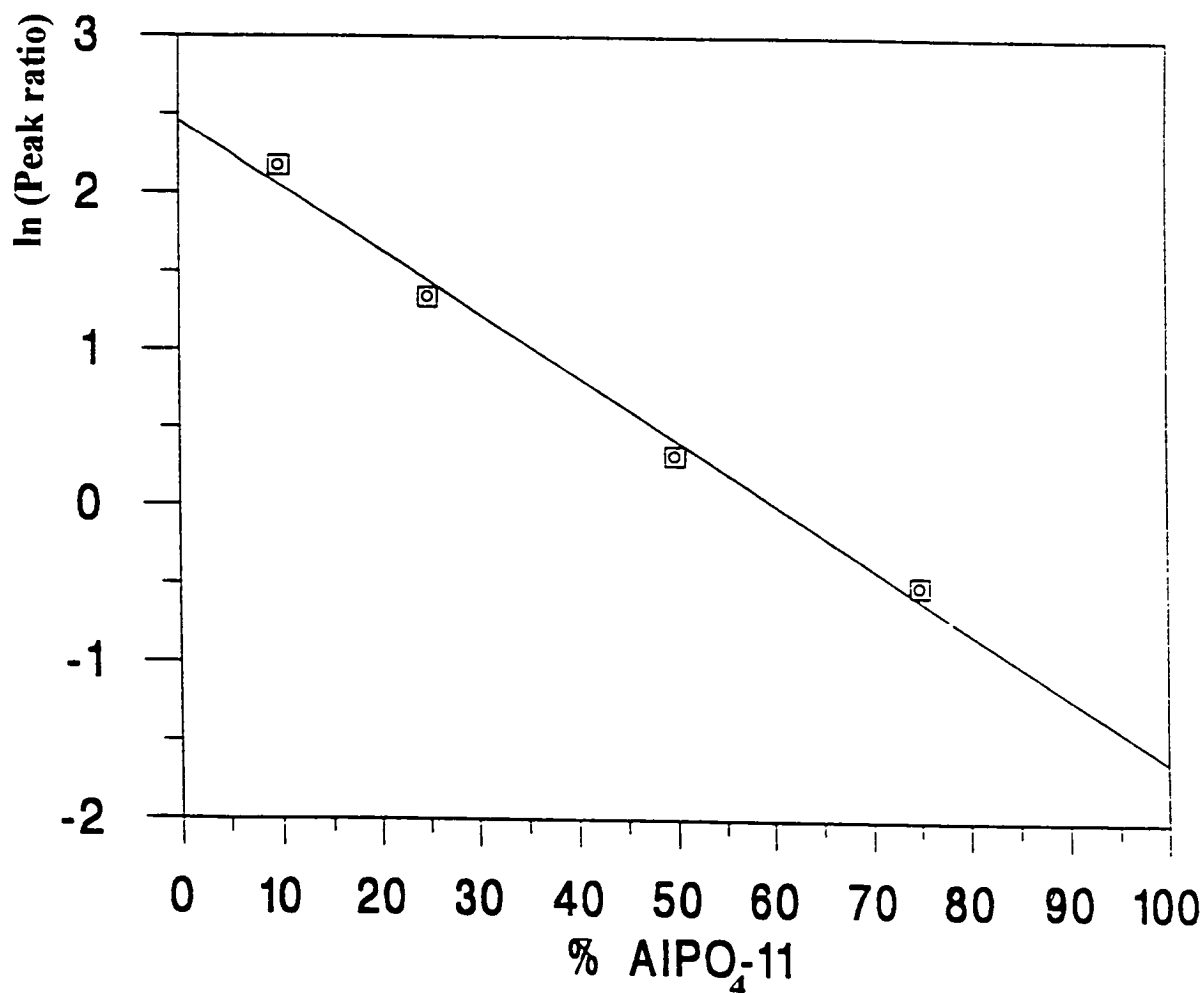
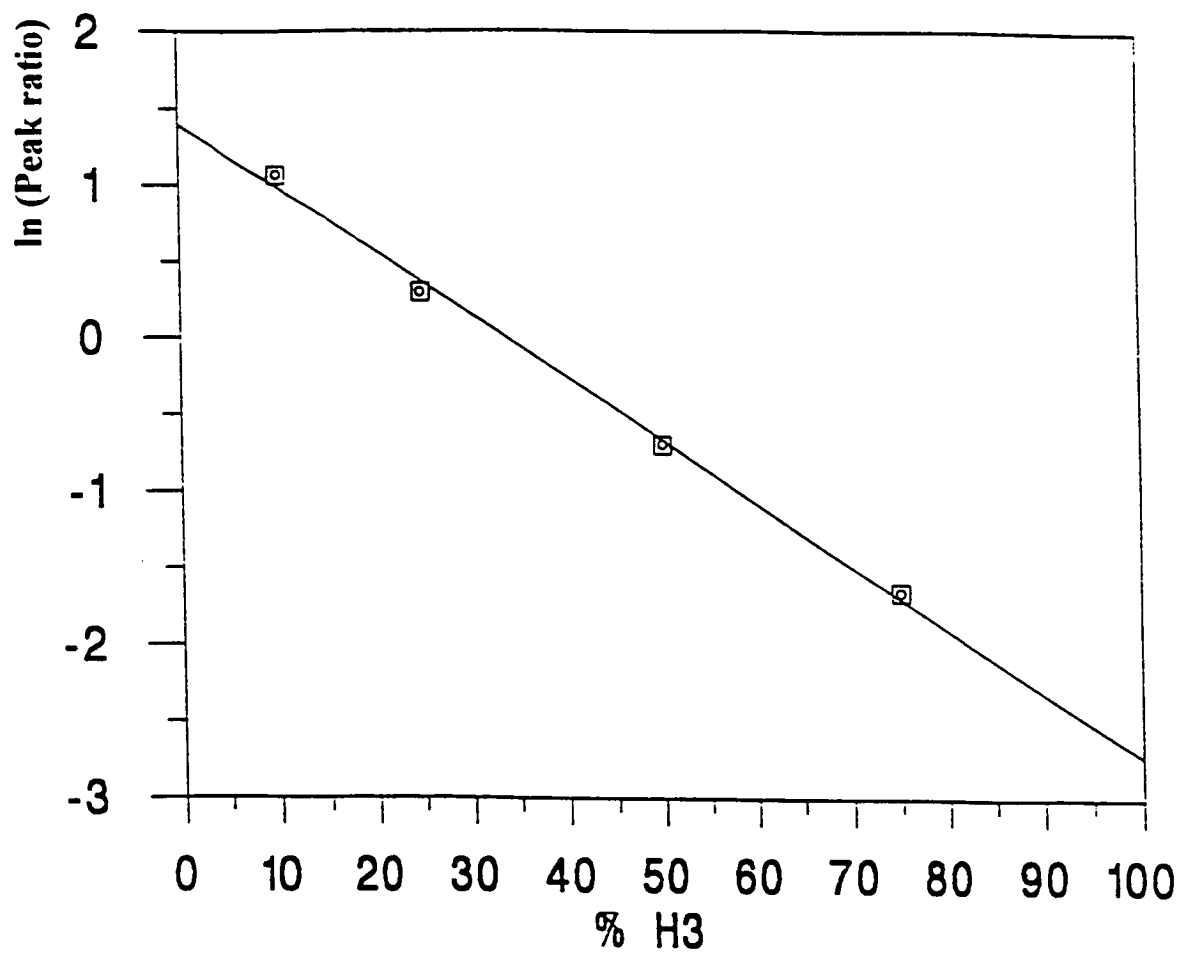


Figure 3.5 Calibration plot of H3 content in VPI-5



3.3 Results

3.3.1 Synthesis from Gels which Contained DPA

An XRPD pattern of the material synthesised in the initial reaction (VS1) is shown below (Fig. 3.6). As can be seen, the product is mainly VPI-5 with what appeared to be a small amount of $\text{AlPO}_4\text{-11}$ impurity.

The XRPD pattern of the product from a second synthesis (VS2) carried out under the same conditions, but with a slightly longer second ageing step (1.75hours), is also shown. The $\text{AlPO}_4\text{-11}$ content of VS2 is similar, though slightly higher than that of VS1. The impurity levels were estimated at 10-15%. Others who followed exactly the procedure of Davis *et al.* also reported that there were usually small amounts of $\text{AlPO}_4\text{-11}$ in the product [13].

Figure 3.7 shows an electron micrograph of the typical wheatsheaf shaped cluster associated with VPI-5.

Table 3.1 compares the XRPD data of VS1 and VS2 with VPI-5 produced by Davis *et al* as well as with the main peaks of $\text{AlPO}_4\text{-11}$ (see Fig 3.1 for XRPD pattern of $\text{AlPO}_4\text{-11}$). The structures of both materials (VPI-5 and $\text{AlPO}_4\text{-11}$) were shown in chapter 1.

The comparison of XRPD data clearly shows that the impurity present in VS1 and VS2 is $\text{AlPO}_4\text{-11}$. It should be noted that the $\text{AlPO}_4\text{-11}$ peaks at 2θ values of 22.15 and 22.6 cannot be seen, despite their large size in relation to other $\text{AlPO}_4\text{-11}$ peaks. This is due to the presence of large VPI-5 peaks at those positions. The levels of impurity were thought to be low enough for the samples to be used in further work. It was later seen, however, that the amounts of $\text{AlPO}_4\text{-11}$ were in fact higher than originally estimated (see section 3.3.2). Yields for VS1 and VS2 were approximately 10g of crystalline product from 60g of gel: Assuming a 25% water content in the crystalline product, this was a yield of approximately 55% of available AlPO_4 . The yields compared well with the amount of product obtained by Davis *et al* [1].

Figure 3.6 XRPD patterns of the products from VPI-5 syntheses 1 and 2 (VS1 & VS2)

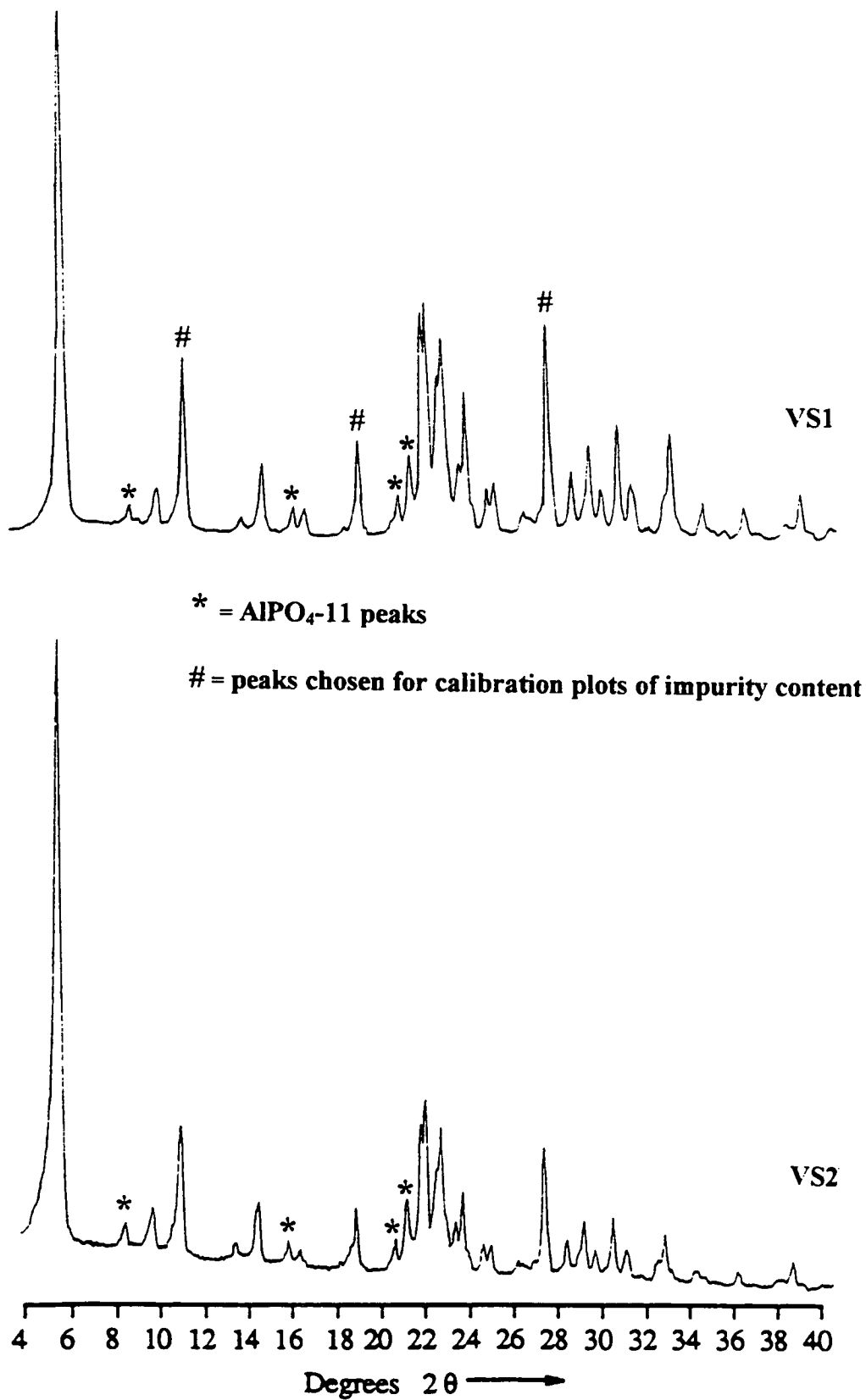


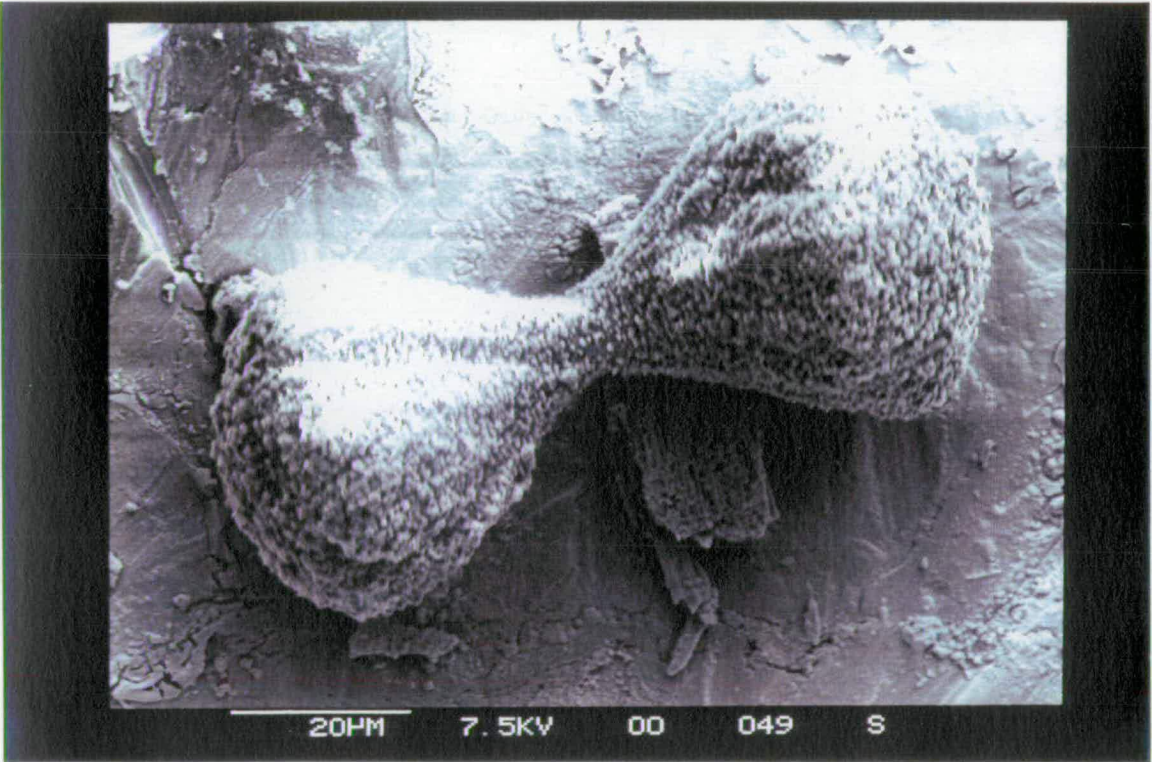
Table 3.1 Comparison of the Peak Positions and Relative Height Ratios in XRPD Patterns of VPI-5 [2], VS1, VS2, and $\text{AlPO}_4\text{-11}$ ^a

VPI-5		VS1		VS2		$\text{AlPO}_4\text{-11}$	
2 θ	I/I _o	2 θ	I/I _o	2 θ	I/I _o	2 θ	I / I _o
5.38	100	5.4	100	5.4	100	-	-
-	-	8.1	4	8.1	5	8.1	33
9.32	2	9.35	8	9.3	8	9.4	53
10.75	14	10.75	36	10.8	22	-	-
-	-	13.25	3	13.3	4	13.3	22
14.26	6	14.25	14	14.3	11	-	-
-	-	15.6	6	15.6	4	15.7	38
16.16	2	16.1	5	16.1	3	-	-
18.68	6	18.65	20	18.7	11	-	-
-	-	20.45	6	20.5	6	20.5	51
-	-	21.0	11	21.0	12	21.0	100
21.76	20	21.6	36	21.7	25	-	-
21.92	22	21.85	38	21.9	29	-	-
22.39	14	22.3	23	22.4	sh	22.15	56
22.56	15	22.55	31	22.6	24	22.6	71
-	-	23.2	sh	23.3	9	23.2	74
23.59	10	23.55	26	23.6	12	-	-
24.46	4	24.45	6	24.5	6	-	-
Note ^b	-	24.8	7	24.8	6	-	-
26.12	2	26.05	3	26.0	3	-	-
27.17	16	27.15	42	27.2	3	-	-
28.19	5	28.15	10	28.2	7	-	-
28.96	7	28.95	16	29.0	10	-	-
29.48	4	29.45	6	29.4	5	-	-
30.28	8	30.20	20	30.2	10	-	-
30.88	5	30.80	9	30.8	6	-	-
32.71	7	32.6	20	32.6	8	-	-
35.86	3	35.8	6	35.8	4	-	-

^a Note that only those lines with $I/I_o > 20$ have been shown.

^b This line was not noted by Davis *et al* [2], but was seen by subsequent workers [17].

Figure 3.7 A typical wheatsheaf of DPA-VPI-5.



As was said earlier, it was seen that the material produced in reaction VS2 contained two visibly different phases. The use of a 30mesh (0.5mm) sieve removed a large proportion of the hard amorphous material and thereby decreased impurity levels. It is thought that the amorphous material was formed when synthesis gel on the sides of the PTFE liner dried out. Careful loading of bombs seemed to limit the amount of amorphous material, as did routine sieving of products. Figure 3.11, section 3.3.2 shows more fully the effects of sieving on purity of VPI-5.

Shorter Reaction Times

Syntheses of VPI-5 were repeated, with no change to the procedure other than that shorter reaction times were used. The reactions are detailed in Table 3.2, along with details of the first two reactions. Note that the impurity levels reported in Table 3.2 derive from the use of the calibrated standards and that this led to an increase in the estimated AlPO_4 -11 contents of syntheses VS1 and VS2 over what had originally been estimated.

Table 3.2 The effects of reaction times upon product purity of VPI-5 synthesised at 142°C.

Run No	Time/hr	Impurities	% impurity
VS1	23	AlPO_4 -11	21
VS2	23	AlPO_4 -11	29
VS3	20	AlPO_4 -11	9
VS4	22	AlPO_4 -11 / TR ^a	24 / trace
VS5	18	AlPO_4 -11	5
VS6 ^b	6	AlPO_4 -11	2

^a TR = AlPO_4 - Tridymite

^b Prior to sieving of the product.

As can be seen from the table, reaction time made a huge difference to the purity of the product. The rate of formation of AlPO_4 -11 seemed to accelerate rapidly around the 20hour mark. It should be noted that the impurity levels of the products from VS5 and VS6 were later lowered by methods described below.



Lower Temperature Reactions

This set of reactions combined shorter reaction times with lower temperatures in an attempt to further improve the purity of the VPI-5 produced. Conditions and results are shown in Table 3.3.

Table 3.3 Effects of lower temperatures upon product purity.

Run No	Temp./ °C	Time / hr	Impurities	% Impurity
VS7	136	5.25	H3 / AlPO ₄ -11	18 / 19
VS8	138	5	H3 / AlPO ₄ -11	50 / 10
VS9	140	5	H3 / AlPO ₄ -11	60 / 20

These results showed that a lower temperature was not the answer to impurity problems with this synthesis system. AlPO₄-11 impurity levels were lowered, though not eliminated, at the expense of high levels of H3. H3 is supposed to be the low-temperature overrun product and so its appearance was not unexpected.

The persistence of AlPO₄-11, however, was initially a surprise in view of the work of Davis *et al*, which suggested that it was a high-temperature overrun product. It was thought that there may have been a difference between the reaction conditions used here and those used by Davis *et al*, which predisposed the Edinburgh system to AlPO₄-11 formation. However in a later paper it was acknowledged that AlPO₄-11 formation could in fact occur at 142°C [3]. Other workers also reported the appearance of both H3 and AlPO₄-11 in VPI-5 syntheses [13].

Since the results indicated that AlPO₄-11 formation had not been suppressed and that low temperatures led to much H3 formation, no further low temperature syntheses were carried out: DPA templated VPI-5 reactions were thereafter only carried out at 142°C.

Further Work on the improvement of VPI-5 Synthesis

In order to try to further improve the purity of VPI-5 produced from DPA templated gels, reaction times at 142°C were lowered still further. Details of the reactions are set out in table 3.4. Note that all of the reaction gels were still of the same composition as that described in section 3.2.1.

Table 3.4 Experimental conditions for shortened reaction times at 142°C

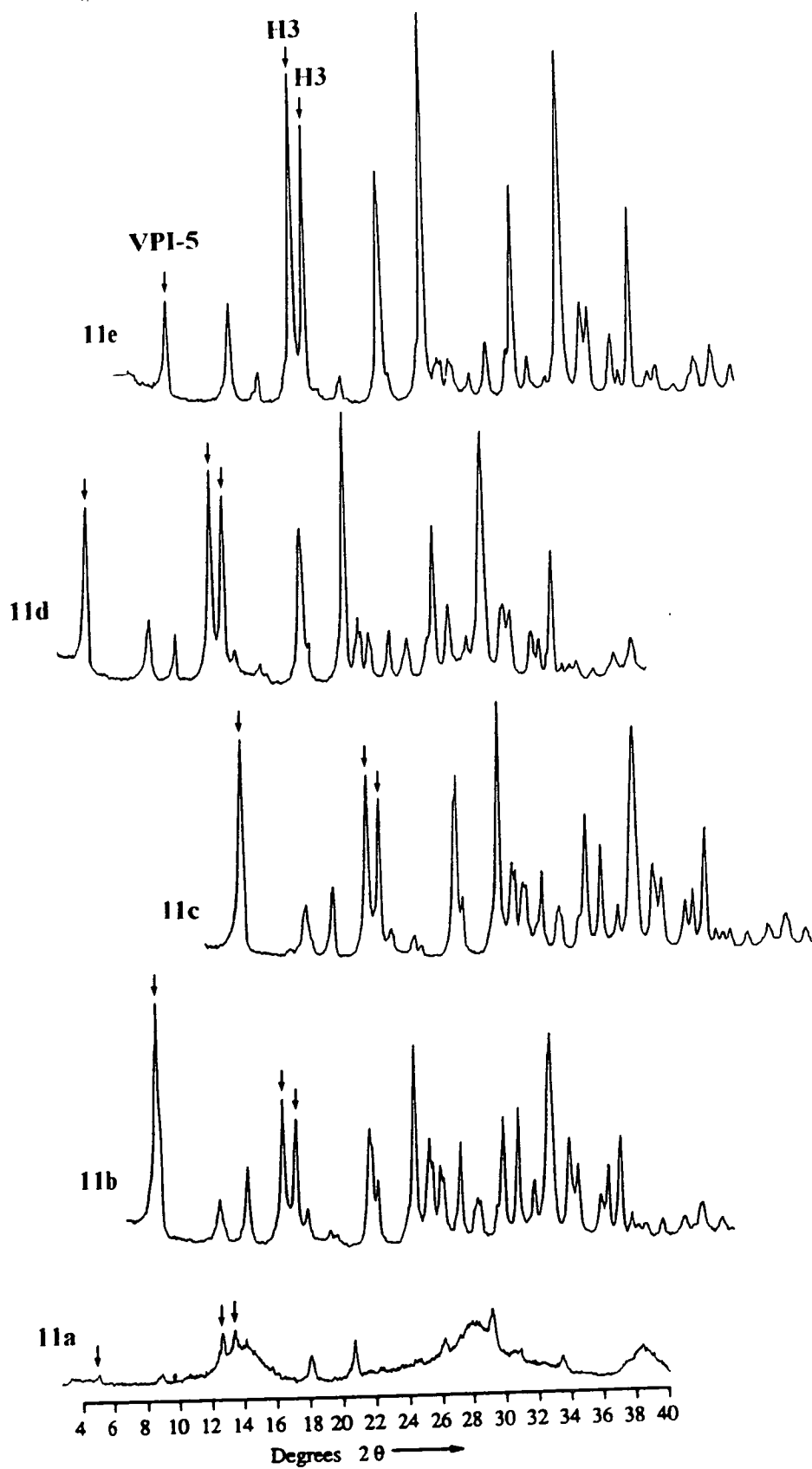
Reaction	Bomb Size	Time/ hr	Impurities
VS10a/b/c	Sm Parr	3 / 3.5 / 4	AlPO ₄ -11 / H3
VS11a/b/c	Sm Parr	1.25 / 2 / 2.75	H3
VS11d/e	Lg Parr	2.75 / 3.75	H3

Despite the short reaction times, all of the products from this set of reactions were still fairly contaminated with impurities. The best product from reaction 10 contained 10% AlPO₄-11 and a trace of H3 as impurities, whilst those from reaction 11 contained mainly H3 as their impurity, ranging from 40% to 80%.

Figure 3.8 shows the XRPD patterns of the products from VS11, with key peaks marked. The XRPD of the product from reaction 11a shows that H3 formation had started after only 1.25 hours, with very little VPI-5 yet formed. After 2 hours (reaction 11b) the amounts of both VPI-5 and H3 had increased and so it seems that H3 is not strictly an overrun product, but that its formation can, under the right (or wrong!) circumstances occur whilst VPI-5 crystallisation is still under way. H3 seemed to continue to form once VPI-5 had ceased to do so since reaction 11c has a higher VPI-5/ H3 ratio than 11b and the same is true for reaction 11e versus 11d.

By analogy with earlier work these reactions should have had very low levels of impurity due to the short heating times. That this was not so suggested that some factor had promoted the synthesis of impurities. The procedure had not altered and bombs had been scrupulously cleaned between reactions, therefore it was suspected that there had been a source of contamination. The source of contamination was suspected to be the alumina source since it was stored in an open box and thus was susceptible to contamination from airborne particles.

Figure 3.8 XRPD patterns of the products from reaction VS11



New Alumina Sources

The next, and final, set of reactions made use of a new batch of Kaiser alumina to eliminate the problems just described. These experiments also looked at the effect upon product of two different ovens, the second of which was a Gallenkamp 300 series, which, when set to the same temperature as the Perkin-Elmer precision oven, was known to cause variation in reaction products, all other factors unchanged. Both sizes of Parr bomb (23 and 105ml) were used also. All reactions were carried out at 142°C and it was the same thermocouple probe which was used to check that oven temperatures were correctly set. The details of the reactions are set out in Table 3.5, below. There was a small amount of work to look at the effect of using Catapal alumina, whose significance was described in section 3.2.1.

Table 3.5 Reaction conditions used with new alumina sources

Reaction	Bomb Size	Time	Oven Used	Alumina Source
12a/b	Sm Parr	3.5/15.5 hr	Gallenkamp	Kaiser
12c	Sm Parr	3.5 hr	Perkin Elmer	Kaiser
13a/b/c	Sm Parr	1/2/2.5 hr	Perkin Elmer	Kaiser
13d/e/f	Sm Parr	1/2/2.5 hr	Gallenkamp	Kaiser
13g/h	Lg Parr	2/2.5 hr	Gallenkamp	Kaiser
14a/b	Sm Parr	50/70min	Perkin Elmer	Kaiser
14c/d	Sm Parr	50/70min	Perkin Elmer	Catapal A
14e/f	Sm Parr	50/70min	Perkin Elmer	Catapal B
15a/b	Sm Parr	55min	Perkin Elmer	Kaiser
15c	Sm Parr	55min	Perkin Elmer	Catapal B

All crystalline products were sieved (see section 3.3.2) and the different size fractions analysed by XRPD. Analysis showed great improvements in the purity of products produced from this batch of reactions, compared to those produced previously. The

products from small Parr bombs were seen to be of better purity than those from large Parr bombs and so, after reaction 13 only small Parr bombs were used.

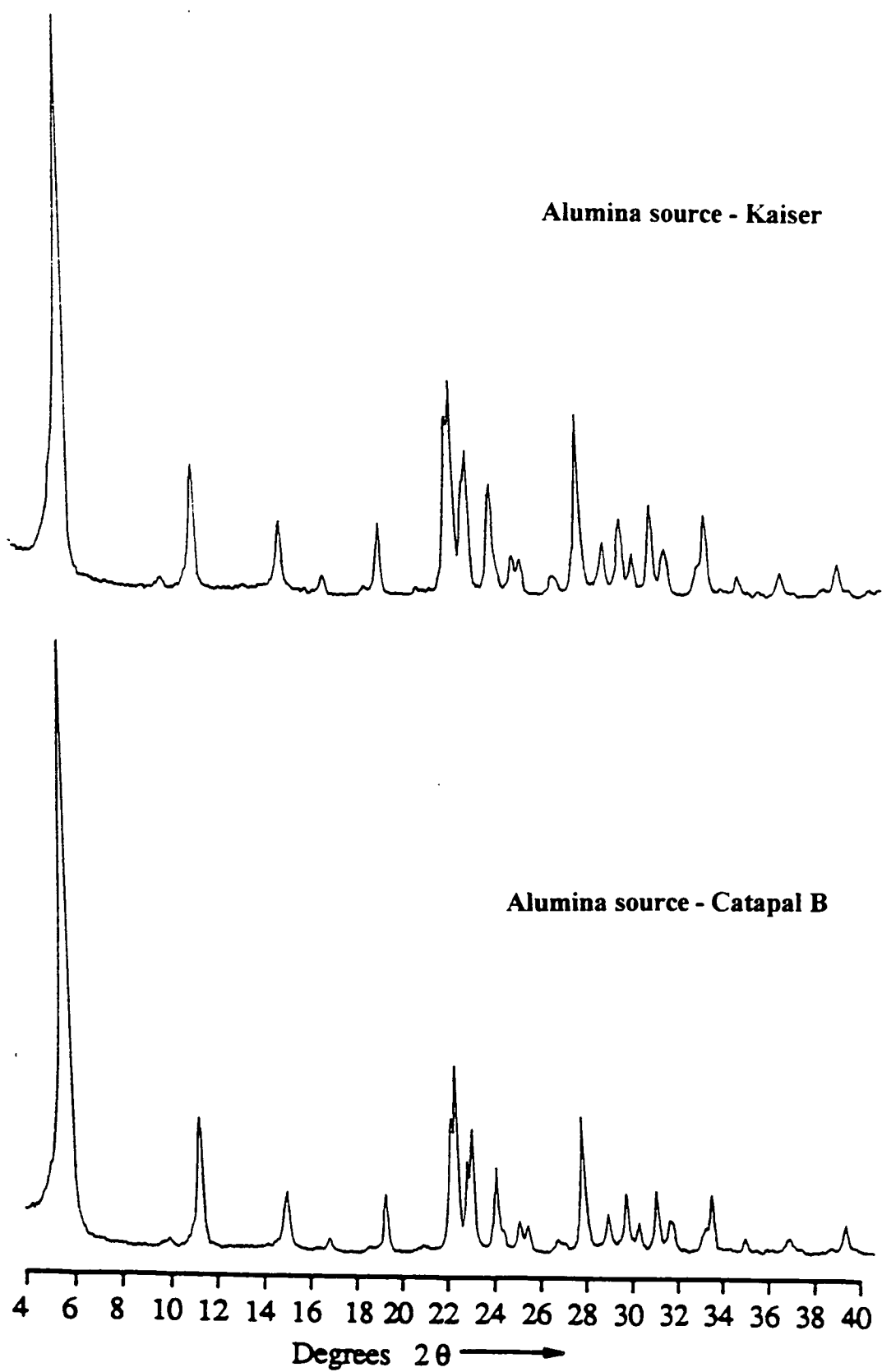
Refinement of the reactions had led to the synthesis of some very high purity samples: All samples synthesised for 50 or 55 min contained either trace quantities of impurity, too small to *quantify*, or else contained no visible signs of impurity whatsoever. The XRPD patterns of some of these are shown in Figure 3.9.

Comparison of Kaiser and Catapal Aluminas. Experiments 14 and 15 showed little visible difference in the VPI-5 produced by the different alumina sources, and as can be seen from Fig.3.9, there was little difference in the purity of product. Thus, with regard to DPA templated VPI-5 synthesis, it can be said that choice of alumina source has little effect on the reaction products.

Comparison of the Different Ovens. The two types of oven used in this work were both very accurate convection ovens, their temperatures were readily held to within less than 1°C of that to which they had been set. However under the reaction conditions used the Perkin Elmer ovens were seen to produce a better product than the Gallenkamp ovens. An investigation showed that crystallisation tended to occur more quickly in the Perkin Elmer oven and that the products from the Gallenkamp oven were more prone to containing H3 impurity and so further reactions only made use of the Perkin Elmer ovens.

These differences may be attributable to the different sizes of the ovens and their methods of temperature control, which affected the way in which the bombs were heated. What was important was that the chosen oven (the Perkin Elmer) gave reproducible results.

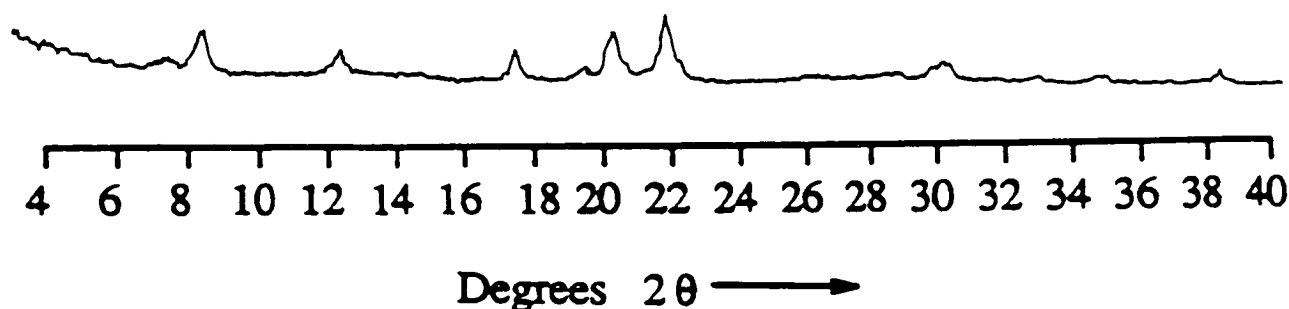
Figure 3.9 Samples of pure VPI-5 synthesised with different alumina sources



3.3.2 Post-Synthesis Treatment of VPI-5

Schmidt *et al* [13] claimed that many of the impurities produced in the VPI-5 synthesis formed as very small crystals which could be removed with the supernatant whilst products were washed straight after synthesis. In order to investigate whether this method would work, less time was allowed for crystals to settle before the supernatant was decanted off from the products of VS5. This produced a cloudy supernatant which was left to clear, after which the solids were collected, dried and examined by XRPD. The solids which were recovered amounted to 0.25g and consisted mainly of AlPO_4 -11, with a small amount of H3, there was no VPI-5 seen in the pattern. Therefore this method of product improvement was adopted for all future syntheses. Figure 3.10 shows the XRPD of the decanted material.

Figure 3.10 Impurity removed by decantation of slurried bomb contents



Sieving. As has already been described, samples were sieved through a 30mesh sieve to remove any large lumps of amorphous material which may have formed. The products of VS6 were more extensively sieved to see how much particle size affected impurity content. A number of different sieves were used in order to separate the products of VS6 into the following size ranges: >1mm; 0.5-1mm; 0.25-0.5mm; <0.25mm. All of the samples, including the small crystals from the washes, were analysed by XRPD. Table 3.6 details the weight and composition of each fraction.

Table 3.6 Constituents of the size fractions of VS6

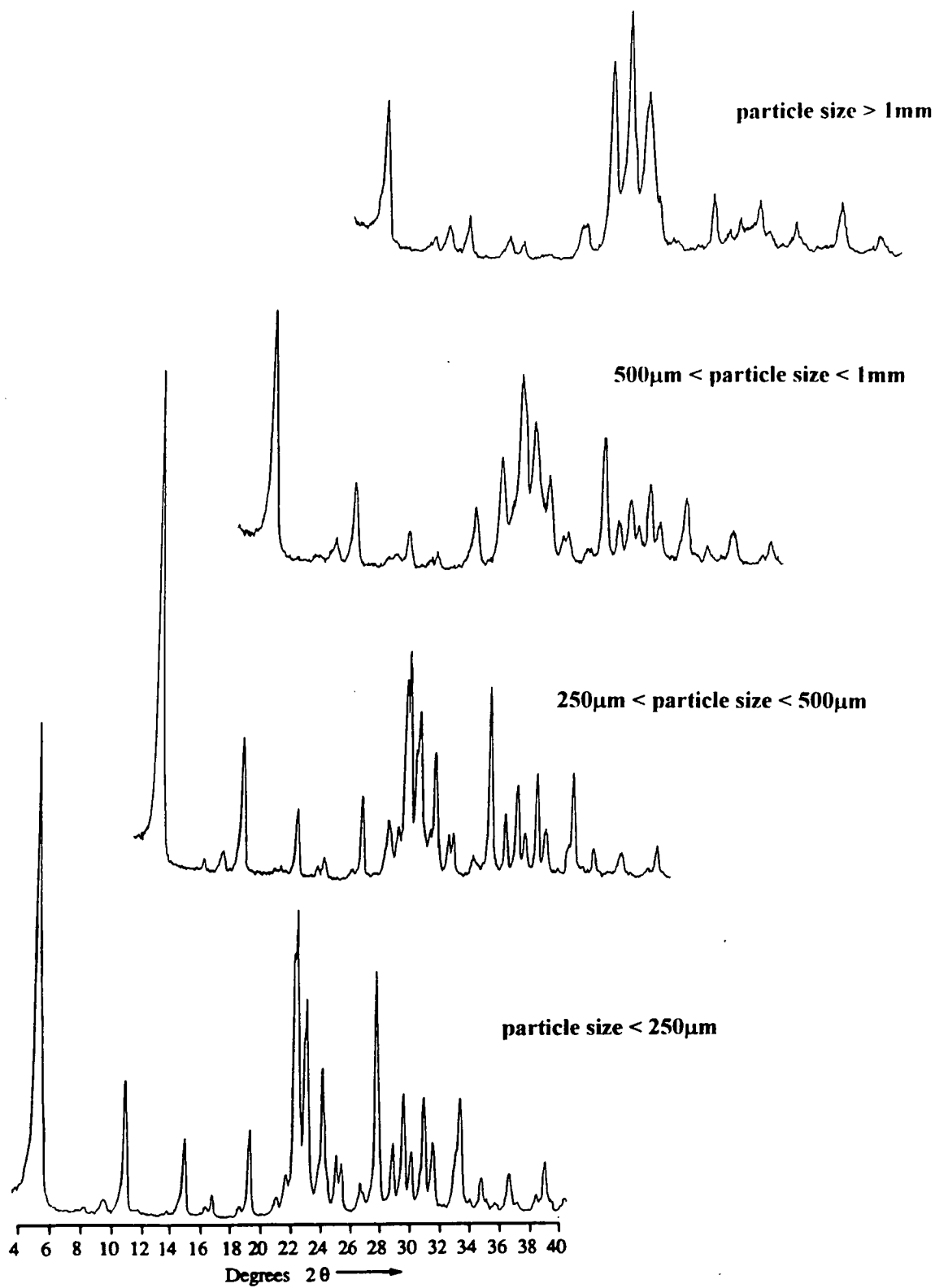
Fraction Size (diameter)	Mass of Fraction	Composition
>1mm	0.06g	Mainly Tridymite, with some VPI-5 and $\text{AlPO}_4\text{-11}$. ^a
0.5-1mm	0.08g	Mainly VPI-5 and Tridymite, with some $\text{AlPO}_4\text{-11}$. ^a
0.25-0.5mm	0.55g	Mainly VPI-5, 10% $\text{AlPO}_4\text{-11}$ and a trace of Tridymite.
<0.25mm	8.5g	VPI-5 with some $\text{AlPO}_4\text{-11}$ (1%).

^a The lack of a good tridymite standard prevented a qualitative assessment of its levels. When there were high levels of Tridymite it was not possible to estimate $\text{AlPO}_4\text{-11}$ levels.

As can be seen from the table and from the XRPD patterns shown in Figure 3.11 there was a large difference in phase composition between the differently sized fractions. This work showed how the removal of the larger particles from the product of VS6 (which amounted to 7.5% of the amount of recovered product) led to much improved purity in the final product. Note that the smallest particles had been removed by decantation of partially settled slurry immediately after synthesis.

The products from all future syntheses were sieved to remove particles >0.25 mm in size or even >0.15 mm in size and it was found to be a very good method of improving purity.

Figure 3.11 The effect of sieving upon the purity of VPI-5 (VS6)



The effect of hot water on VPI-5. Fig.3.12 shows the XRPD patterns of VPI-5 after treatment with hot water. The VPI-5 was stirred in boiling water for 9 hours or Soxhlet extracted with hot water for the same time. As can be seen the VPI-5 structure was still intact after the treatments. The reason for such treatment was that it had been claimed to improve the stability of VPI-5. Further work to investigate the effects of these treatments upon the thermal stability of VPI-5 is detailed in chapter 4.

3.3.3 Use of different Templates to Synthesise VPI-5 from Gels

Several attempts were made to synthesise VPI-5 from gels which contained TiPOA and TMAOH, with the composition described in section 3.2.1. The work followed that of Davis and Young [3] in which such a composition was said to produce VPI-5 which was not only free of H3 impurity, but which was also more stable than that which was produced from DPA-templated gels. The work of Davis and Young was followed very closely, but to no avail. Reactions were carried out at temperatures of 141, 142 and 150°C, in 23ml Parr bombs at autogenous pressure. As with Davis and Young, final pH values of 7-8 were observed for all samples, however, as can be seen from the XRPD patterns in Figure 3.13, the products were heavily contaminated with H3, even when only partially crystalline.

It was suggested that the problem lay in the alumina source, for it was Kaiser alumina which had been used, but Davis *et al* had used Catapal B, which has the same pseudoboehmite structure as Kaiser alumina, but which is supposed to have a different microcrystallinity. Therefore Catapal B was used, in 142°C syntheses, but still the products contained large amounts of H3, as shown in Figure 3.14, and so synthesis from the TiPOA / TMA system was abandoned. Other workers suggested that the source of the amines could affect the outcome of syntheses [14].

Figure 3.12 The effect of hot water upon VPI-5

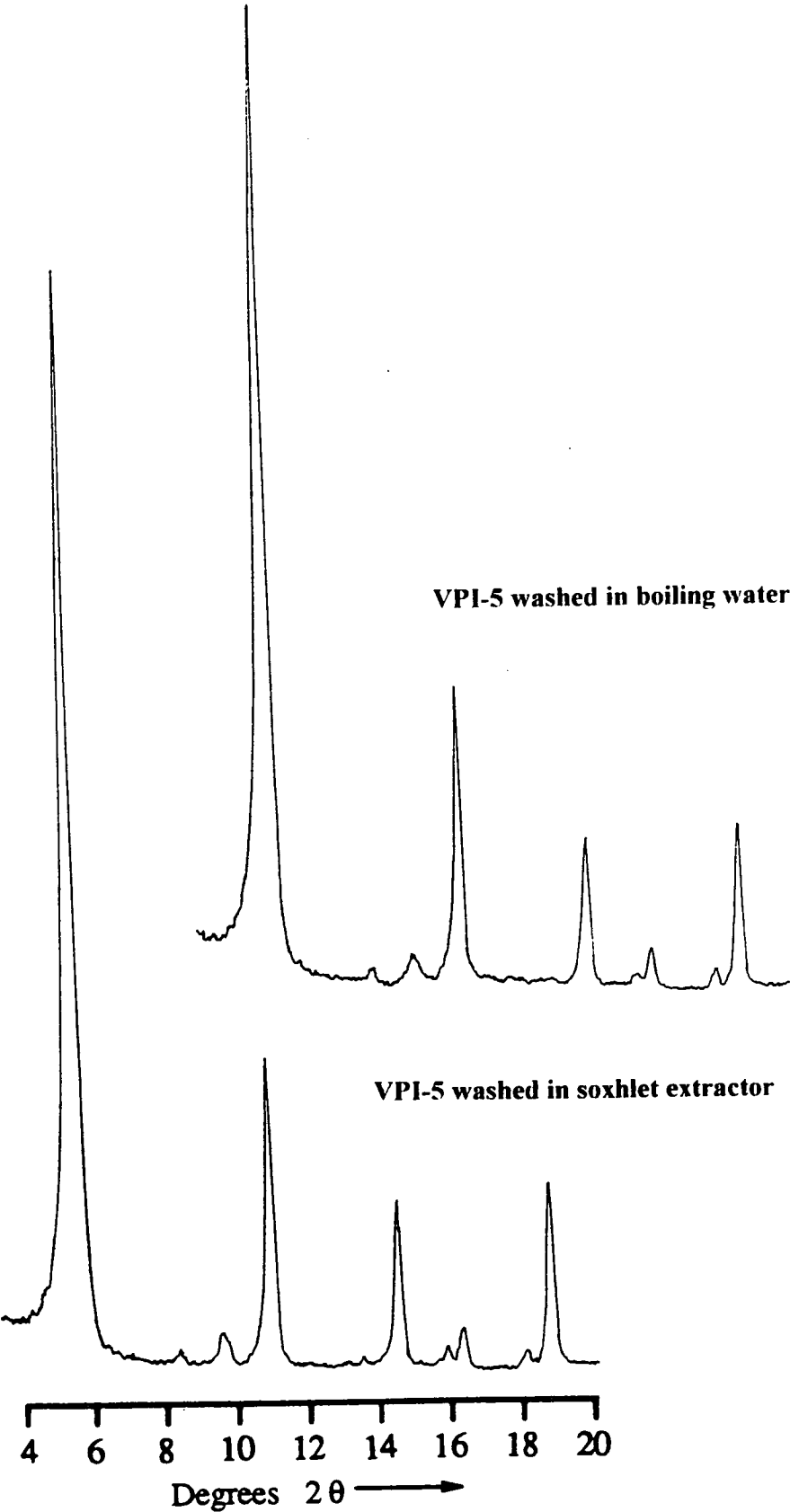
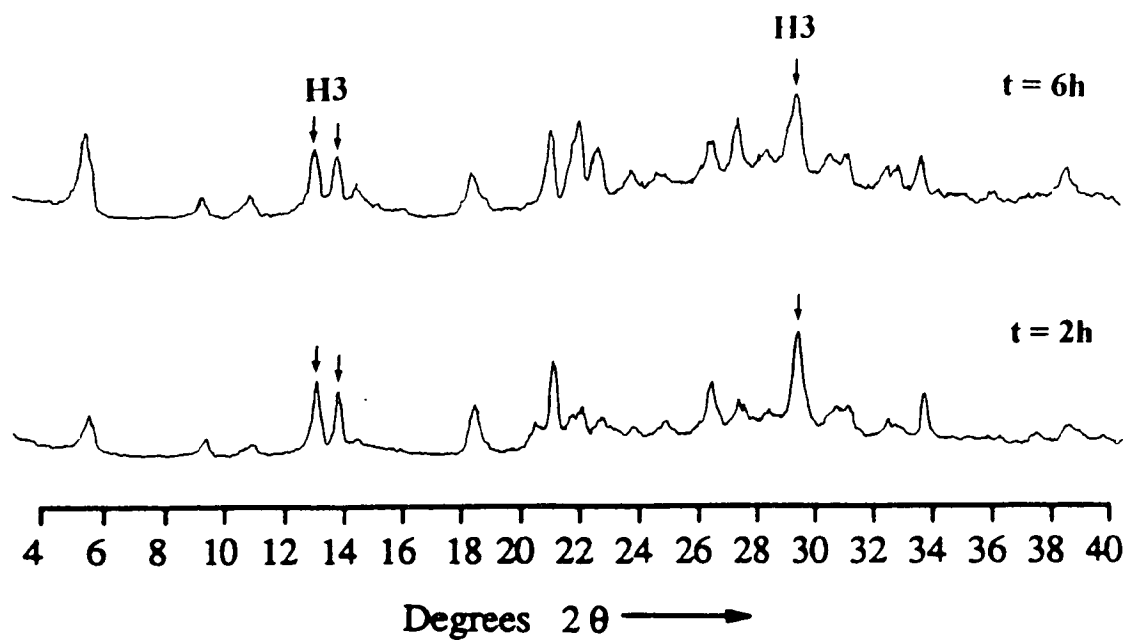
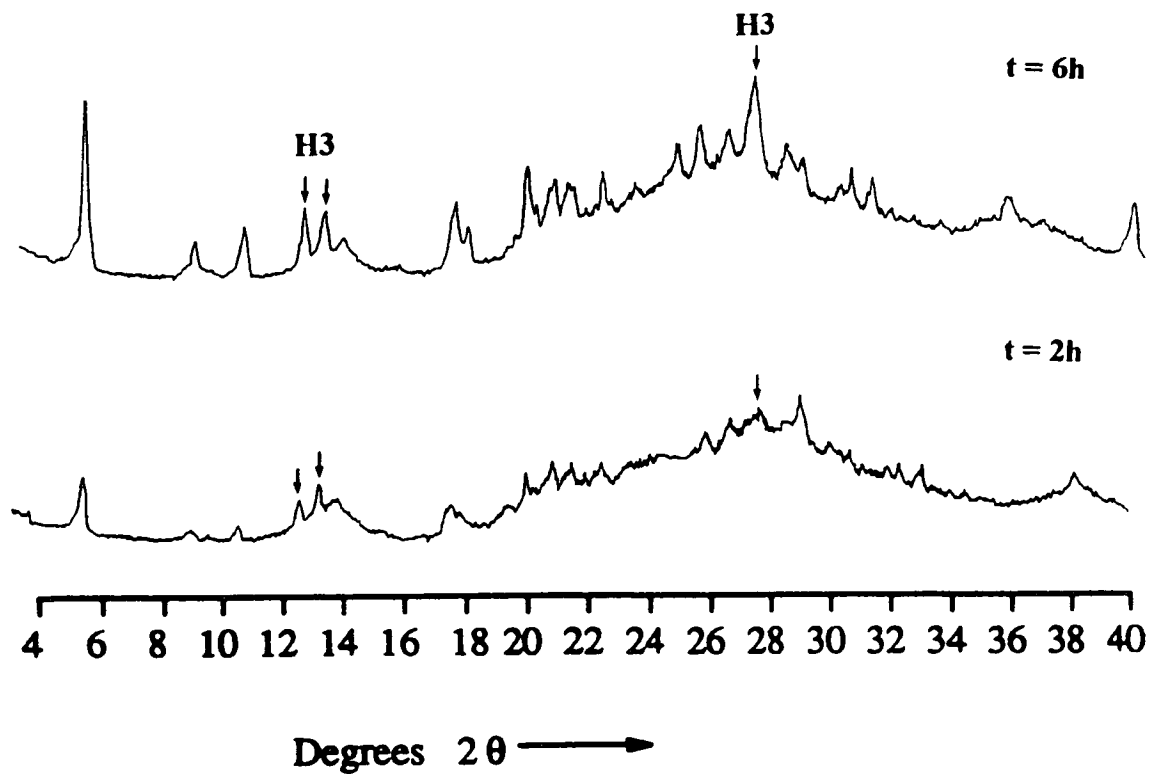


Figure 3.13 Products of TiPOA/TMAOH syntheses with Kaiser alumina**Figure 3.14** Products of TiPOA/TMAOH syntheses with Catapal B alumina

3.4 Synthesis of VPI-5 from a Precursor Complex

3.4.1 Background

As has been said, the first syntheses of VPI-5 to be reported used reaction mixtures which contained either amines or quaternary ammonium salts [1]. However little or none of these organic compounds were occluded in the crystalline product [3]. This unusual feature [4], together with the hydrophilic nature of VPI-5 [14] and its subsequent identification as a hydrate [18, 19] suggested that the organic additives were not acting directly as templates or void fillers but were instead mainly influencing the water structure and solution chemistry of the reaction systems. It was not unexpected, therefore, when two routes were reported which did not synthesise a material corresponding to VPI-5 in the conventional way, but which used template-free systems [20, 21].

K.C. Franklin had investigated clear solution synthesis of VPI-5 from a soluble inorganic precursor [21]. This section describes further extension of the work of Franklin in order to improve his method and produce a supply of good quality material. This enabled work to be undertaken to see if the material made by this route had better properties of uptake and stability than the VPI-5 which was produced by the DPA route.

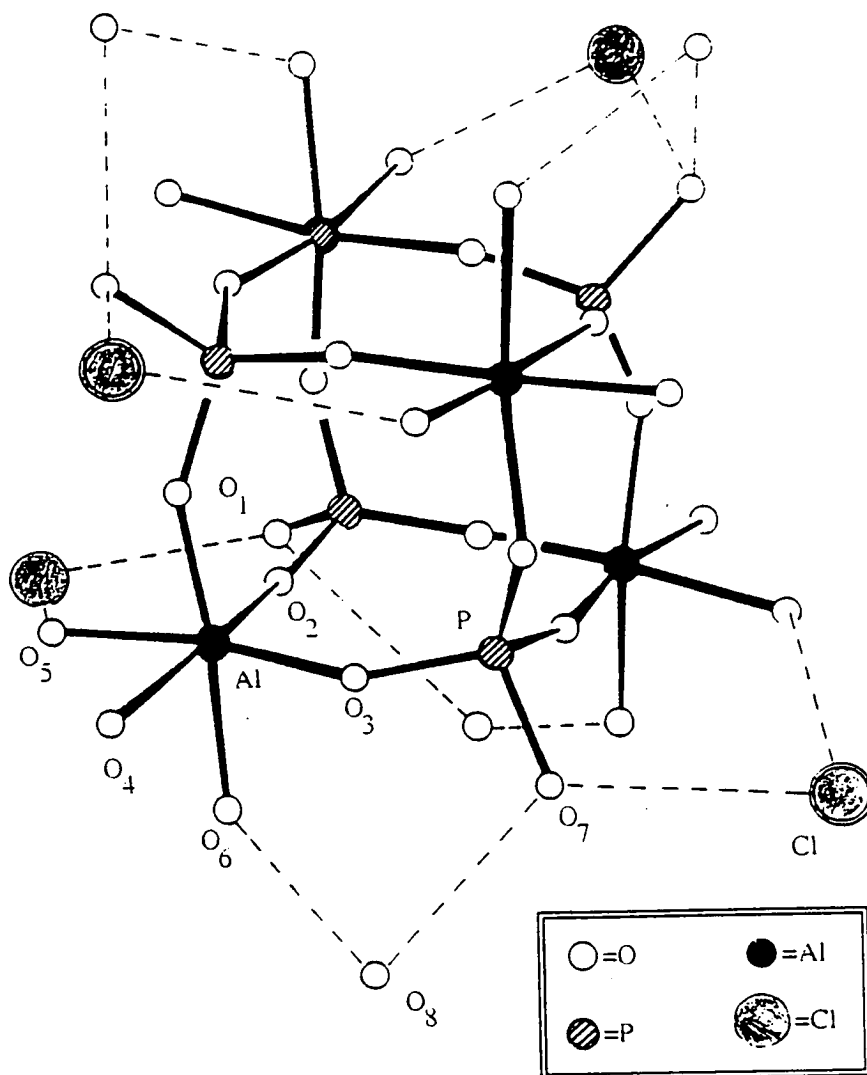
The precursor which was used by Franklin was Aluminium phosphate hydrochloride ethanolate (APHE), whose empirical formula is as follows:



It is a tetrameric solid whose structure, Figure 3.15, shows it to consist of an approximately cubic cage, with octahedral Aluminium and tetrahedral Phosphorus atoms at alternate vertices linked to each other by bridging oxygens along the cube edges. The cubes are linked through ethanol ligands, and chloride ions hydrogen bonded to protonated phosphate oxygens. The complex was first reported in 1969 [22, 23] as a precursor for the preparation of refractory binders and surface coatings, and its characterisation was detailed in 1975 [24].

Figure 3.15

Perspective drawing of one of the tetrameric units of APHE [24].



$O_1 - O_3$: Bridging oxygens
in cage structure.

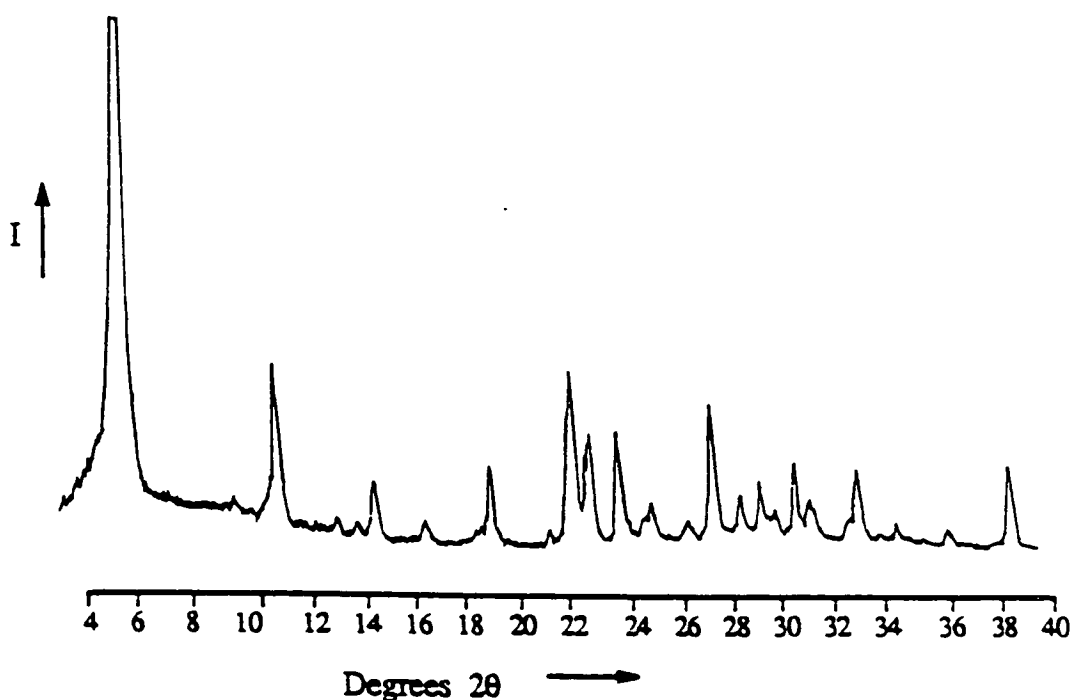
$O_4 - O_6$: oxygens of ethanol
ligands.

O_7 : non bridging oxygen (terminal)

O_8 : oxygen of loosely bound ethanol
----- hydrogen bonds

With the advent of AlPO_4 molecular sieves, the cubes were seen as potential building blocks for several known and proposed AlPO_4 structures. Franklin discovered that dissolution of APHE in water, followed by heating in a sealed system yielded, when the correct conditions were obtained, a good sample of what appeared to be VPI-5, its XRPD pattern is shown in Figure 3.16. There is some debate as to whether the product of an organic-free system should be referred to as VPI-5 or as H1, and, indeed, as to whether VPI-5 and H1 are the same, or different materials. The reasons for this will be discussed at the end of the chapter, but for the purposes of this work the product which attempts were made to synthesise will be referred to as VPI-5.

Figure 3.16 XRPD of APHE-VPI-5 synthesised by Franklin [21].



The correct conditions for synthesis of VPI-5 from APHE solutions appeared to be a small window of time and temperature. Attempts to improve the APHE system to produce pure samples of VPI-5 are described in the following section. Also described is work which stemmed from this, when it was discovered that the VPI-5 produced from APHE often formed as discreet, fairly large needles (up to 30 μm long). Such a morphology is different from that seen in VPI-5 produced by templated gels, which occurs mainly as wheatsheaves of small needles (Davis *et al* [2] also claimed that

DPA-VPI-5 can form as spheres of 5µm in diameter). The work attempted to capitalise on the tendency for APHE -VPI-5 to form a single needles by synthesising a single crystal of VPI-5 which would be large enough for a single crystal study.

3.4.2 Synthesis of APHE

APHE was synthesised according to the method described in the initial patent [22], which was:

1. Anhydrous AlCl_3 (40g) was dissolved in dry Ethanol (300ml) and cooled over ice.
2. Phosphoric acid (18.4ml, 85% solution) was added slowly (40min) with stirring.
3. The white, crystalline solid which formed was filtered off, washed with a small amount of dry ethanol, and dried over P_2O_5 in a slightly evacuated dessicator. It was important that the desiccator was not evacuated thoroughly, as APHE decomposes over time to form amorphous Aluminium phosphate, HCl and ethanol, and this process is accelerated by exposure to low pressure.

3.4.3 APHE / Water System

The system from which Franklin synthesised VPI-5 [21] consisted solely of APHE dissolved in water and heated: initial work therefore concentrated on the optimisation of that system. An initial advantage which the APHE synthesis held over previous syntheses was that the reaction mixture did not require ageing, all that had to be done was to dissolve APHE in water and fill reaction vessels with the requisite amount of solution.

Franklin had reported that the synthesis of the sample of VPI-5 (Fig. 3.16) which contained very low levels of impurity was from a reaction which was heated at 116°C for 4 hours and so this was taken as the starting point for the investigation. For that synthesis a TOM had been used as the reaction vessel whilst, in order to get reasonable yields, most of the reactions detailed here were done in 23ml Parr bombs. Each bomb was loaded with 13ml of APHE solution, carefully measured out to ensure consistency between reactions. Temperatures from 114-120°C were investigated, for a range of times. As before all bombs were carefully washed to reduce the likelihood of seeding between reactions.

Some reactions were also done in sealed melting point tubes in order to allow a large number of reactions to be studied in a short space of time. Although melting-point tubes did not produce enough sample to enable XRPD analysis of the products, a good idea of what had formed in the tubes was gained by analysis of the sealed tubes under an optical microscope. The tubes were held in drilled out aluminium blocks which meant that they could be kept hot whilst transferred from oven to microscope and, if looked at quickly, returned to the oven still hot for further reaction to take place.

3.4.4 Attempts to Synthesise a Single Crystal of VPI-5

As was mentioned, VPI-5 synthesised from an APHE solution occurs mainly as single needle-shaped crystals or as bundles of a few needles. Although several detailed powder-diffraction studies of VPI-5 have been carried out [17, 18, 25, 26], no one has yet succeeded in producing a crystal of VPI-5 which is large enough for a single-crystal X-ray diffraction study. Such a study would yield more information about the structure of VPI-5. Attempts were made to synthesise such a crystal by alteration of the conditions used to synthesise VPI-5 from a solution of APHE.

The first method which was used to try and produce large crystals was to increase the viscosity of the reaction solution, in order to retard crystal settling [27]. This was mainly so that crystals would have access to nutrients for longer, rather than settling on the bottom of the reaction vessel where nutrients would be scarce, and also to make it less likely that crystals which started off single would grow into aggregations with other crystals. Polyethylene glycol 6000 (PEG 6000) was used to get the increased viscosity. This long chain polymer exists as a solid at room temperature, which easily dissolves in water to produce viscous solutions. It was hoped that PEG 6000 would not interfere chemically with synthesis and that the long, tangled polymer chains would not be trapped in large quantities in the pores of VPI-5: Certainly previous aluminophosphate syntheses, those of JDF-20 [28] in which smaller glycols have been used in the solvent have not shown glycol to be present in the pores after synthesis. Syntheses were carried out with a range of PEG 6000 concentrations and, hence, solution viscosities. Melting-point tubes and TOMS were used for these syntheses.

Another approach to the problem of growing a large crystal was to seed the gels with small needles of VPI-5 which had been made previously. There were two ways in which this was done, firstly small amounts of seed were used, equivalent to about 5% of the expected yield, and secondly large amounts of seed were used, equivalent to about 100% of expected yield. The first method was designed to produce secondary nucleation, whilst the second method attempted to encourage growth upon the seeds. Franklin's studies [21] as well as those of Szostak *et al* [29] appeared to show that the product crystallised from solution rather than from an amorphous intermediate. This increased the likelihood of producing a large crystal from a seeded solution since lack of need for an intermediate stage meant that seeds could start growing immediately rather than have to wait for the gel to age and so allow other nuclei to appear. Prior to use, seed crystals for the 100% method were cleaned and divided by ultrasonic agitation of a suspension, followed by decantation of the supernatant after only a short settling time so that very small crystals were discarded. For the 5% method crystals were merely ground. All seeded reactions were done in TOMS, which precluded the chance of any other seeding taking place since a new PTFE liner was used each time.

3.5 Results of APHE Work

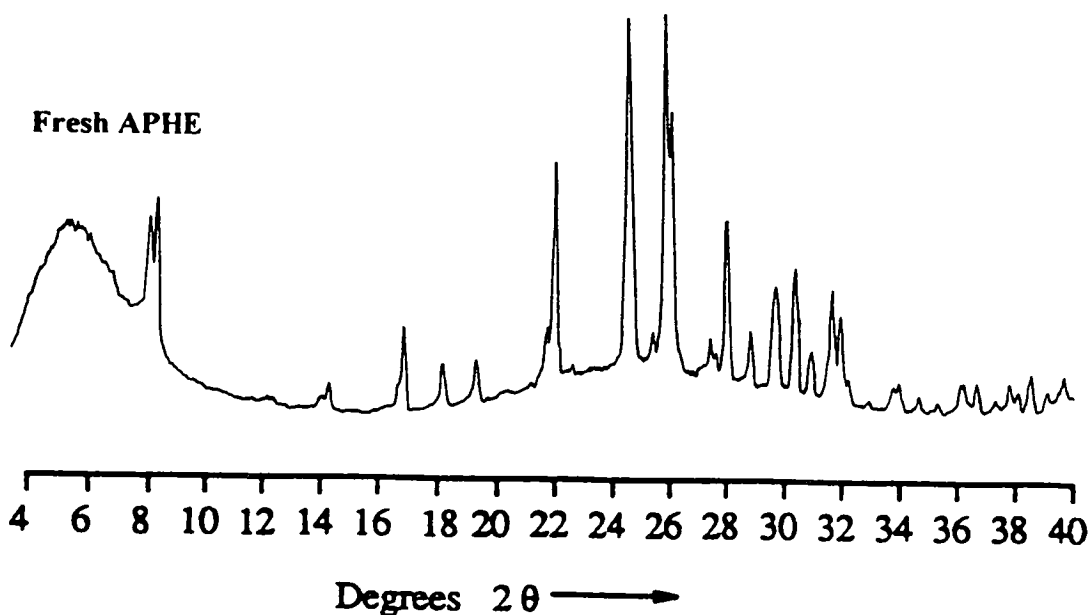
Figure 3.17 shows the XRPD pattern of freshly made APHE itself which clearly shows that there is a crystalline structure. Also shown is an XRPD pattern of APHE which has decomposed to an amorphous state. Care had to be taken to use only good condition APHE, which was distinguished by its soft fondant-like texture from the decomposed material which formed hard lumps.

Figure 3.17 The effect of ageing upon APHE

Old APHE (2 weeks)



Fresh APHE



3.5.1 APHE / Water System

Since the aim of this work was to get the largest yields of the purest possible material, all of the solutions used were made up as 1APHE : 20H₂O, this being the maximum amount of APHE which it was possible to dissolve in cold water. That ratio worked out as 9.63g APHE dissolved in every 10.0g H₂O, which gave an AlPO₄ content of 3.39g per 20g of solution and an ethanol content of 5.11g. Despite the high level of ethanol in the reaction solution it is thought to play little role in VPI-5 formation. Evidence for this came from thermal analysis of APHE-VPI-5. This showed that:

i) The temperature at which weight loss started was the same for APHE-VPI-5 as for DPA-VPI-5 (which contained nothing which was more volatile than water).

ii) There was no visible difference between the TGA trace of as-made APHE-VPI-5 and a sample which had been washed in boiling water. If ethanol had been present in the channels washing would be expected to have removed it thus leading to an altered TGA trace.

These two findings gave strong evidence that no ethanol was present in the channels of APHE-VPI-5, and hence strongly suggested that it did not play a role in synthesis.

As stated previously, reactions were carried out at temperatures between 114 and 120°C. The ovens used were Perkin Elmer precision ovens, each of which held 3 x 23ml Parr bombs. Oven temperatures were recorded throughout the reactions. After removal from the ovens, bombs were immediately quenched in cold water for 6minutes to stop the reaction. The contents were emptied into beakers, given several washes with distilled water, the supernatant being decanted off each time, and the solids were filtered off on 0.8µm filter membranes. All samples were examined by XRPD and by optical microscopy. Results from these reactions are detailed in Table 3.7 and presented graphically in Figure 3.18.

Table 3.7. Products from heated APHE solutions (23ml Parr Bombs; 1APHE : 20H₂O). Note that products are listed in order of their estimated relative amounts, with trace quantities in brackets.

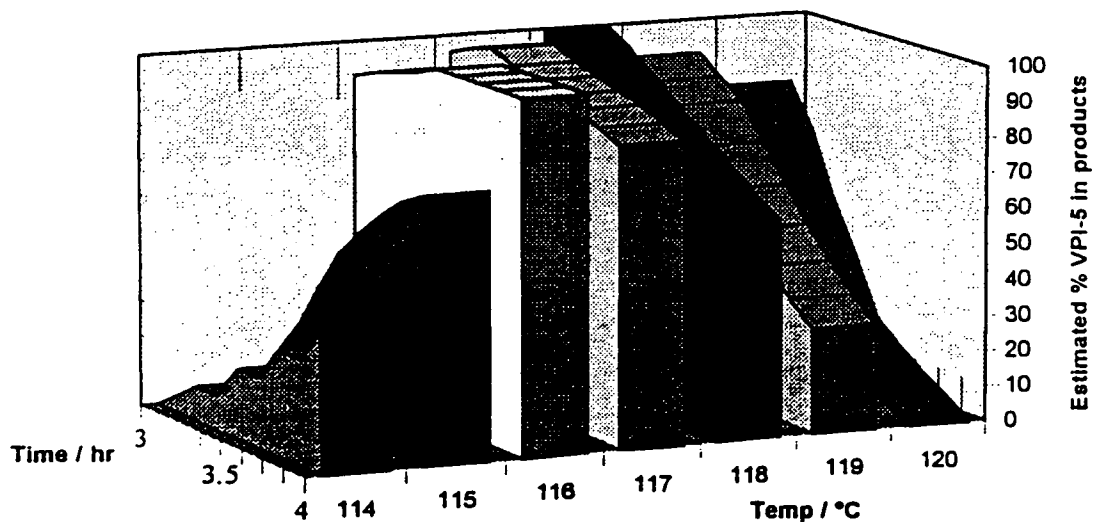
Temp./ °C	t = 3hr	t = 3.25hr	t = 3.5hr	t = 4hr
114	Amorphous	Am + VPI-5	Am + VPI-5	Am + VPI-5
115	-	Am + VPI-5	Am + VPI-5	VPI-5 + Am ^a
116	VPI-5 + Am	VPI-5 + Am	VPI-5	VPI-5
117	VPI-5 + Am	VPI-5	VPI-5 + (H3)	VPI-5 + TR + H3
118	VPI-5 ^b	VPI-5 + H3	VPI-5 + H3 + TR	-
119	VPI-5 + H3	VPI-5 + H3 +TR	TR + VPI-5 + H3	TR + H3 + (VPI-5)
120	VPI-5 + H3	-	VPI-5 + TR + H3	TR + H3

Am = amorphous

^a After 4.5hr; VPI-5 + Am + H3

^b After 2.75hr VPI-5 + Am

Figure 3.18 VPI-5 production from APHE solutions.



These results show just how small the window was in which pure VPI-5 could be synthesised from an APHE solution. At low temperatures pure VPI-5 was never achieved whilst at high temperatures the window of pure VPI-5 was either fleeting or did not exist due to rapid appearance of impurities. It was between 116 and 118°C that pure APHE-VPI-5 could be synthesised. An interesting observation was that single crystals were more prevalent at lower temperatures, i.e. at 116°C most of the VPI-5 appeared to occur as single crystals, whilst at 118°C a lot of the VPI-5 seemed to be bunched into the beginnings of wheatsheaves.

Further synthesis of VPI-5 from this route was done at 117°C, the middle temperature of the window. Figure 3.19 shows an XRPD pattern of the VPI-5 produced at this temperature. As far as can be seen, when the correct conditions were achieved it was pure VPI-5 which was produced, without any need to for such post-synthesis treatment as sieving the product. In this respect the synthesis was superior to that from DPA templated gels, where even the best products still contained traces of impurity. When conditions were not correct, the only impurities which were seen were H3 and tridymite, $\text{AlPO}_4\text{-11}$, the commonest impurity seen in the products of DPA-templated gels, was never seen in the products of APHE solutions.

Where the APHE route was not so satisfactory was in its yields, which were very low. The average yield of VPI-5 from one bomb was 0.3g, which was around 6% of the theoretical maximum, taking into account the fact that around 25% of the product weight was water. When larger quantities of product were obtained it was always because there was impurity present.

It can be seen by reference to Fig. 3.9 that the relative peak heights in Fig. 3.19 are not the same as those seen in the XRPD pattern of VPI-5 produced from a DPA templated gel. This is attributed to orientation effects, since the needle-shaped crystals produced with APHE have an obvious tendency to align themselves lengthways.

Figure 3.20 shows an electron micrograph of the crystals of VPI-5 which were produced from APHE which shows the very different form of the products from APHE compared to those from DPA templated gels. The bulk properties differed greatly also, in that, instead of being a free flowing powder like many crystalline materials, including VPI-5 from DPA gels, the products from APHE aggregate and also occupy a very large volume, so that they appear akin to expanded polystyrene. APHE VPI-5 was in fact nearly impossible to put through a sieve because it clumped together so much. The way that the crystals aggregated, coupled with their small size,

meant that they could not be easily broken up by grinding in order to reduce orientation effects.

The size of the crystals and their purity were so good that a sample of VPI-5 produced from APHE was shown to Dr M.Harding of Liverpool University, who is a leading crystallographer, for advice as to whether crystallography on such a sample might give new information about the structure of VPI-5. Funding has since been gained for analysis of the sample by synchrotron radiation at the ESRF at Grenoble and the results are awaited.

Figure 3.19 XRPD of pure APHE VPI-5

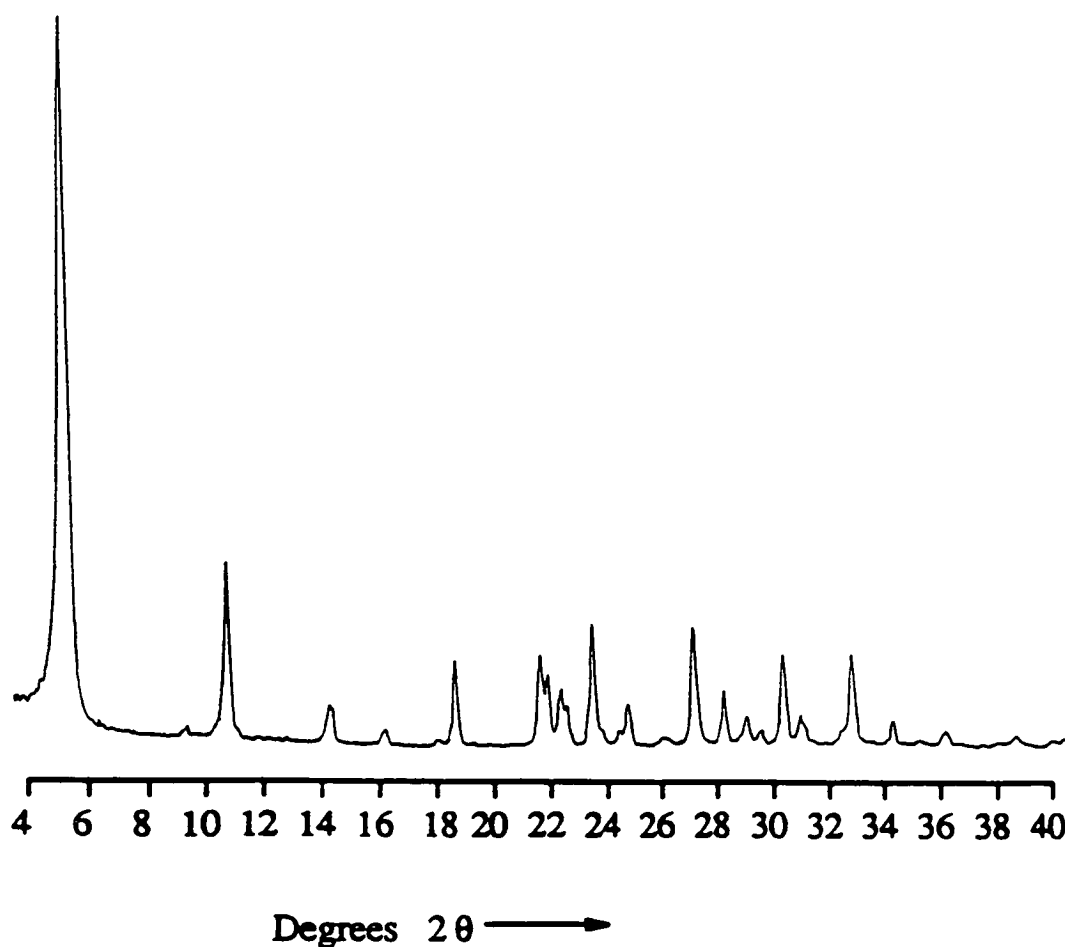
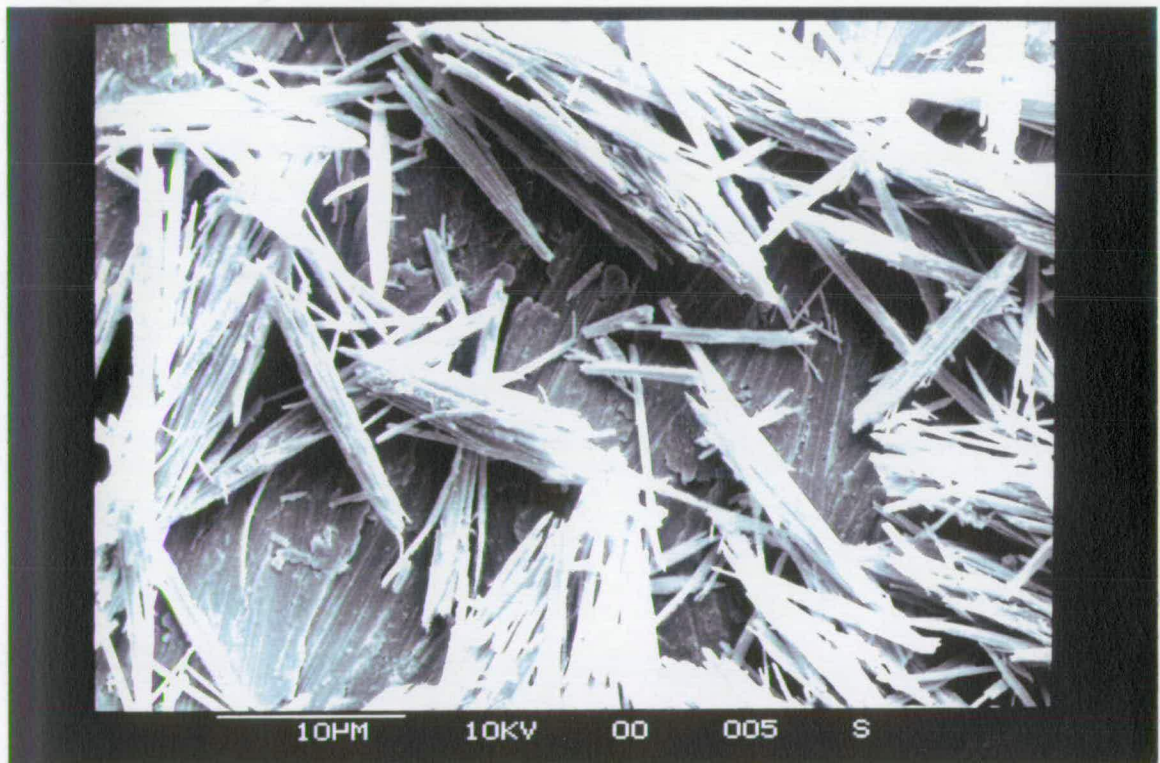


Figure 3.20 Scanning electron micrograph of APHE-VPI-5.



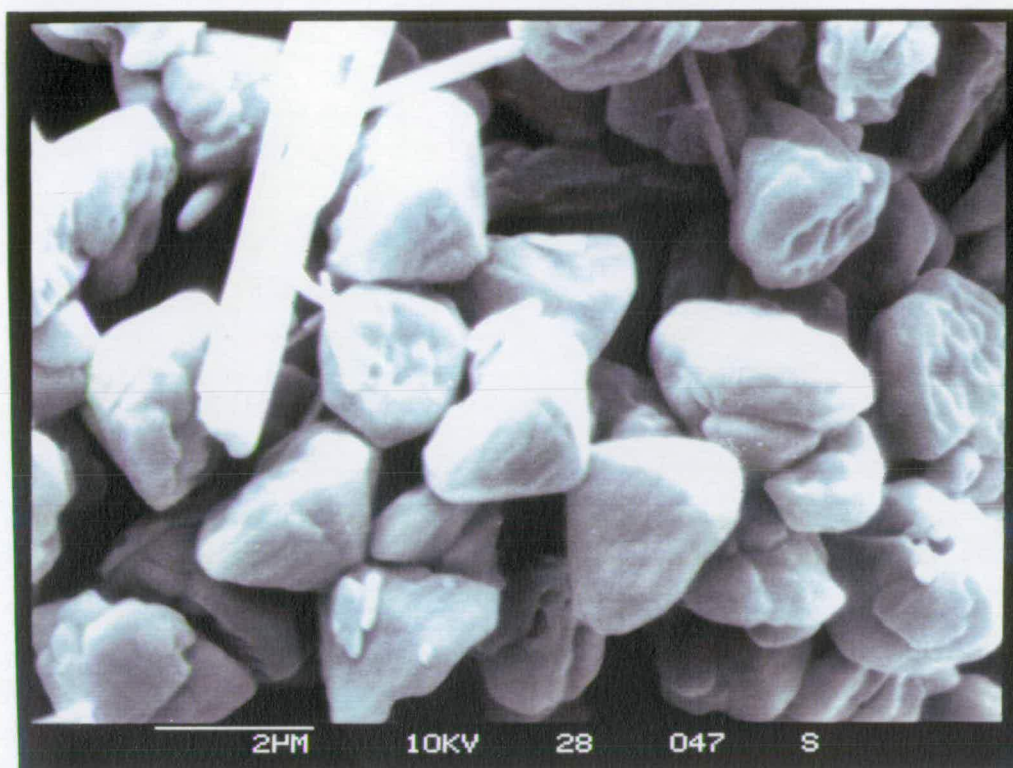
The reactions which were done in melting-point tubes were examined solely by optical microscopy, analysis of the products was, therefore more difficult, especially the identification of the aluminophosphate phase H3, which was the first impurity phase to appear in the synthesis of VPI-5 from APHE solutions. H3, however, seems, from XRPD analysis of the products from bombs, only ever to have occurred as a minor impurity phase in the synthesis of VPI-5 from APHE and was therefore difficult to spot with an optical microscope. The second impurity to be seen, and apparent end product of the reaction, was AlPO_4 -tridymite, which was easy to identify through the microscope from its lozenge shaped crystals which were often twinned, as shown in Figure 3.21. In general, reactions in melting-point tubes were seen to proceed about 30% faster than those done in the Parr bombs. This is attributed to the contents of the tubes reaching temperature much faster than the contents of bombs. Table 3.8 details the observations from a set of reactions carried out at 117°C in melting-point tubes.

TABLE 3.8. Results from heating APHE solution at 117°C in melting-point tubes.

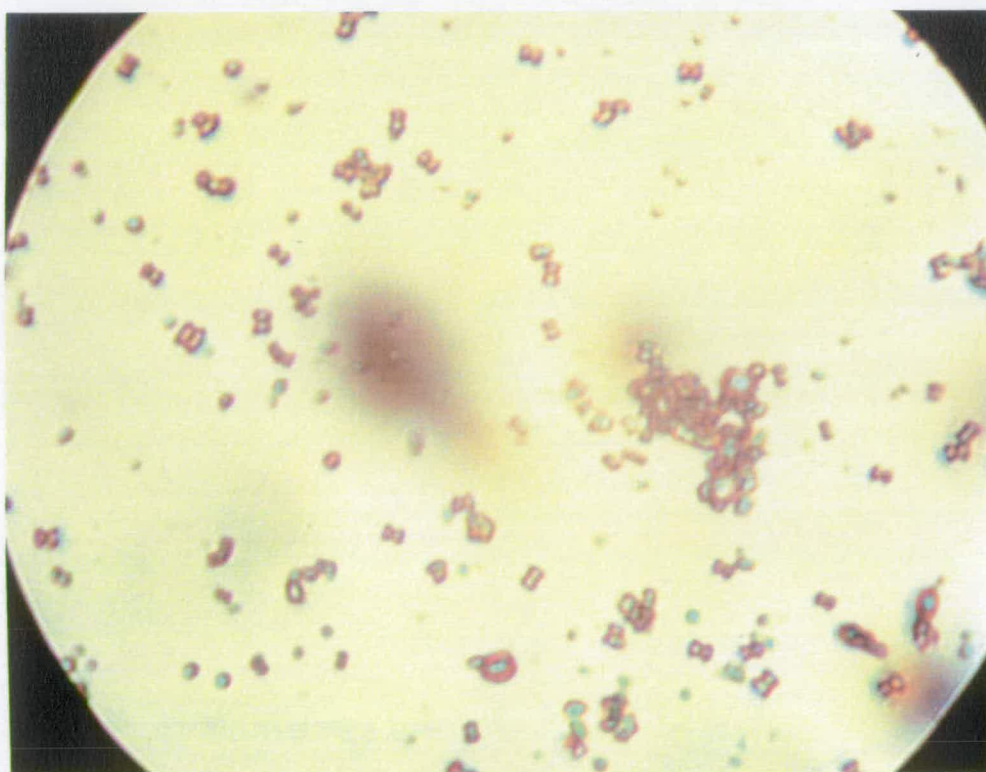
Time	Observations
2hours	Solution was opaque, with a few needles visible.
2hr 20min	Solution less opaque, many needles present.
2hr 40min	Solution more opaque, many needles joined.
3hours	Mixture of opaque areas of settled solids, and clear liquid. A few lozenge shaped crystals of tridymite.
3hr 20min	Solution opaque again. Mainly tridymite crystals, those needles still present looked to be breaking up.
3hr 40min	Clear liquid and settled solids, only tridymite visible.

The above observations certainly show the distinct periods of VPI-5 formation and tridymite formation, and may also show when H3 was formed.

Figure 3.21 AlPO_4 -Tridymite formed from APHE.



An electron micrograph of AlPO_4 -Tridymite.



AlPO_4 -Tridymite viewed through an optical microscope.

The interpretation of the results detailed in Table 3.8 is given below. It should be made clear that the lack of XRPD data for the tube contents means that the interpretation is not necessarily right, but it is based on the best available evidence.

i) VPI-5 was first to form and its small crystallites led to the opaque tube contents seen after 2 hours.

ii) After 2 hours 20 minutes VPI-5 synthesis had stopped or slowed and crystals of VPI-5 were large enough to settle, thus the solution was clearing.

iii) H3 formation occurred briefly around 2 hours 40 minutes and so the solution became more opaque again from suspended crystallites.

iv) VPI-5 and H3 formation had ceased after 3 hours and all crystals had settled to leave a clear solution.

v) After 3 hours 20 minutes tridymite had started to form and so the solution was once again opaque.

vi) Finally, after 3 hours 40 minutes, all crystallisation was complete, only tridymite was now present, any VPI-5 and H3 having recrystallised to tridymite.

Despite the fact that there was not such a clear-cut distinction between steps ii) and iii) as there was between steps iv) and v), these observations fit in so well with XRPD results from bomb syntheses (see Table 3.7) that it seems likely that the H3 step was really there.

Some of the tubes were opened and attempts were made to recover crystals in order to analyse them by XRPD, none of the attempts were successful due to the very small number of crystals produced. In those tubes which were not opened, the crystals, of all types, were seen to dissolve after a few hours of standing, to produce clear solutions. The reason for this is thought to be a lowered pH due the redissolution of HCl which entered the gas phase when the solutions were heated, this accords with the work of Winiecki and Suib [30]. It is thought also, that it is the evaporation of HCl which allows crystallisation to occur in the first place, by causing a rise in pH.

3.5.2 Single-Crystal Growth

Use of Polyethylene Glycol 6000

In order to carry out these reactions, PEG 6000 was first dissolved in distilled water and then the APHE was dissolved. The amount of PEG 6000 in any given reaction solution is stated as a weight percentage of the amount of water that the PEG was dissolved in, e.g. a 25%PEG solution was made with 2.5g PEG 6000 dissolved in every 10g of water. The amount of water in which APHE was dissolved remained constant throughout, e.g. when 25% PEG solutions were used, 19.62g of APHE were dissolved in 25.48g of solution to maintain an APHE : water ratio of 1:20. All reactions were carried out at 117°C.

Initially the reactions were done in melting-point tubes, to enable the size of crystals to be easily followed through the optical microscope. Unfortunately it proved extremely difficult to load melting-point tubes with solutions which were more viscous than 25%PEG. From solutions of 25%PEG or less, the sizes of the VPI-5 needles remained almost the same as those which formed from the APHE / water system, at approximately 20-30 \times 1 μ m. There was one exception to this, when a tube heated for 3 hours was seen to contain 3 crystals whose lengths were about 100 μ m, with diameters of a few μ m. Attempts to isolate these crystals proved unsuccessful.

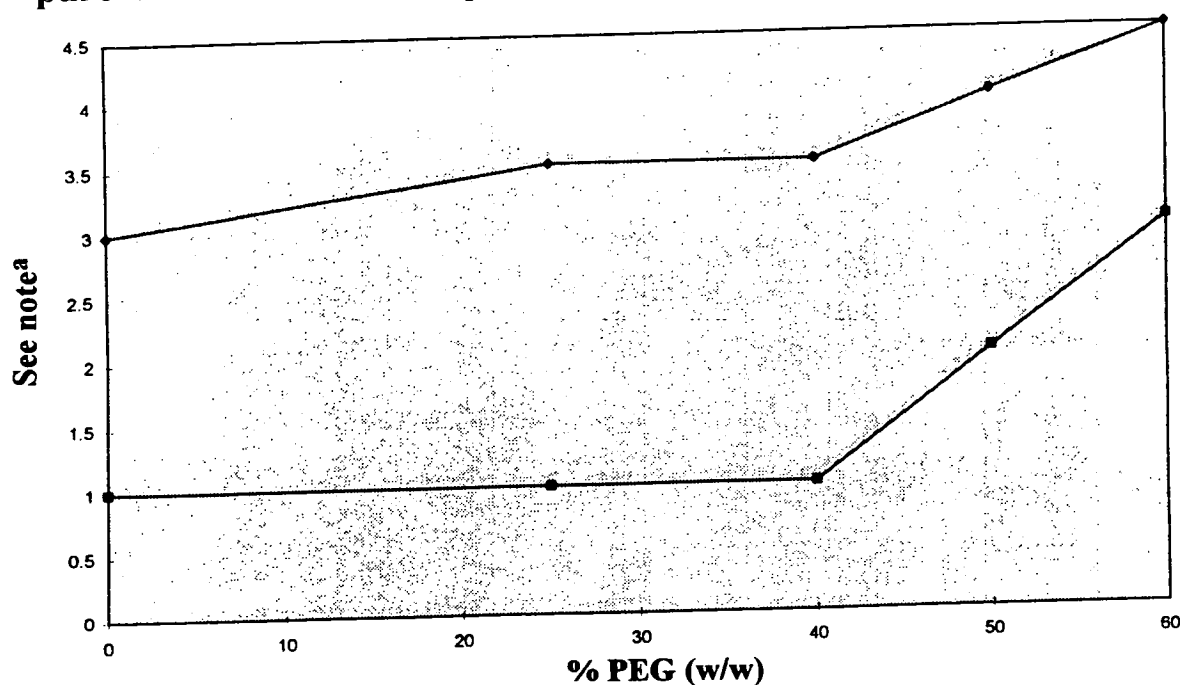
In order to enable more viscous solutions to be used, further reactions were carried out in TOMS. The contents of these could not, of course, be studied *in situ*, however, aside from the ability to use more viscous solutions, they had the advantage of yielding enough product to enable XRPD analysis so that the identity of the products could be known with certainty. As was said earlier, the contents of melting-point tubes redissolved if left for too long, thus the one attempt which had been made to recover large crystals had had to be done quickly. The products of TOMS, on the other hand, were washed, filtered and put onto microscope slides in the search for large crystals and so, if such crystals were to be found, there would be no need to rush their recovery. Solutions up to 60%PEG were used in the TOMS, at higher levels than this it became difficult to get APHE to dissolve. The results are detailed in Table 3.9.

Table 3.9. Crystal sizes and Products from Viscous APHE solutions at 117°C

Time / hr	% PEG 6000	Average Crystal Size / μm	Products seen by XRPD analysis
2.5	0	20 x 0.5	VPI-5 + Am
2.5	25	20-25 x 0.5-1	Am + (VPI-5)
2.5	40	20-25 x 0.5-1	Am (+ VPI-5)
2.5	50	8-12 x 0.5-1	Am (+ VPI-5)
3	0	20-30 x 0.5-1	VPI-5
3	25	20-25 x 0.5-1	Am + VPI-5
3	40	15-20 x 0.5-1	VPI-5 + Am
3	50	10-15 x 0.5-1	Am (+ VPI-5)
3	60	10 x 0.5-1	Am (+ VPI-5)
3.5	0	30-40 x 0.5-1	VPI-5
3.5	25	20-25 x 1	VPI-5
3.5	40	15-25 x 0.5-1	VPI-5
3.5	50	15-30 x 0.5-1	VPI-5 (+ Am)
3.5	60	15-25 x 0.5-1	Am + VPI-5
4	0	40 x 0.5-1	VPI-5 (+ TR)
4	50	30-60 x 1-2	VPI-5
4	60	30-50 x 2-3	VPI-5 + Am

It seems from these results that the effect, at all concentrations, of PEG was to delay the onset of crystallisation of VPI-5. Figure 3.22 illustrates this point with a graph showing the time at which pure VPI-5 was achieved for each of the different PEG concentrations. It was only at its highest concentrations that the presence of PEG had a significant effect upon crystal size. As the plot of maximum observed crystal width (also Fig. 3.22) shows, it was upon the width of the crystals that high concentrations of PEG had greatest effect. This was a significant finding since it is the smallest dimension which is the limiting factor for crystallography. However despite their relatively large size, none of the crystals produced from viscous solutions were large enough for a single-crystal study.

Figure 3.22 The effect of PEG concentration upon the time taken for pure VPI-5 to form and upon crystal width.



—◆— Plot 1 - Time taken for pure VPI-5 to form/ hr

—■— Plot 2 - Maximum observed crystal width/ μm

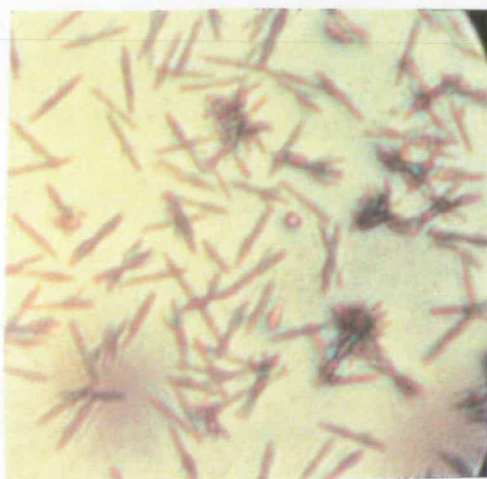
^aThis scale represents time/ hr for plot 1 and size/ μm for plot 2.

In the course of this work crystals which looked to be very long usually turned out, upon closer examination, to have a waist in the centre as if they were in the early stages of wheatsheaf formation. However the crystals from the 50% and 60% PEG solutions were closely examined for signs of waists and, although some were seen, a large number of the crystals appeared to be truly single. Figure 3.23 shows photographs, taken through an optical microscope, of the products from solutions which contained different concentrations of PEG. This figure also shows that besides being waisted, many of the crystals from PEG-free or low PEG concentration mixtures appear to show other signs of wheatsheaf formation whereby small secondary needles are growing from the waists.

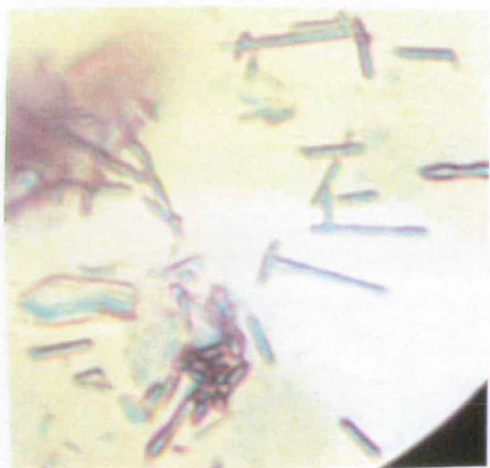
Figure 3.23 Typical crystals of APHE-VPI-5 from solutions which contained PEG



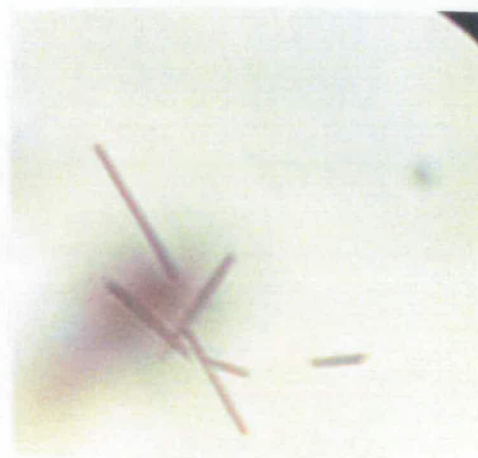
0% PEG



40%PEG



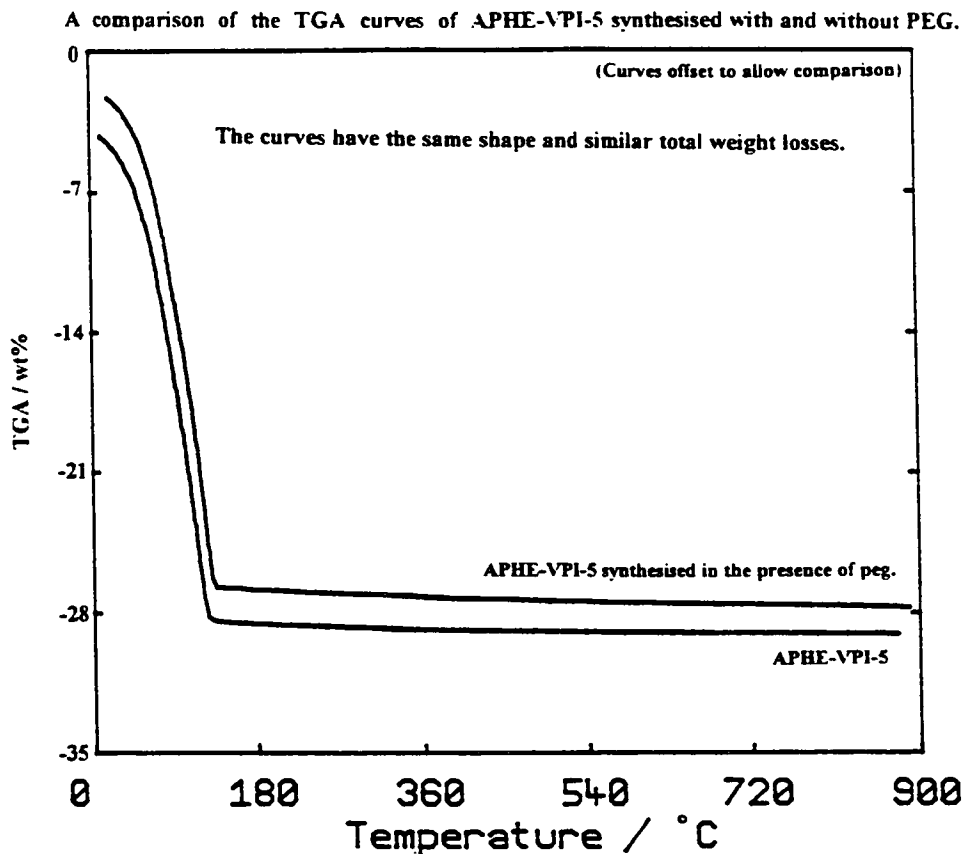
50% PEG



60% PEG

It had been hoped that PEG would act only to increase the viscosity of the reaction solutions and would not be trapped in the pores of VPI-5. In order to try and find out if this was so, highly crystalline samples were thermally analysed. As can be seen from Figure 3.24 these data look very similar to those from VPI-5 synthesised without PEG, with no significant weight loss above 140°C, not what would have been expected if there had been any PEG present in the pores.

Figure 3.24



Use of Seed Crystals

As expected, the use of seeds accelerated the reactions so that initial work, with small amounts of seeds and at the same times and temperatures as unseeded reactions, produced only tridymite. This meant that reaction times and temperatures had to be altered. Best results were obtained at 112°C, at which temperature pure VPI-5 was obtained. There was, however, no great increase in the size of the resulting crystals as compared to those produced in the absence of seeds.

The next approach was to use both seeds and PEG 6000. 50% and 60% PEG solutions were used, with small and large amounts of seed. These methods produced

larger crystals than unseeded reactions but, as can be seen from Figure 3.25, average crystals were not only still too small to be of any use but most were bunched.

Close examination of the products revealed however, that several of the reactions had produced a small number of huge crystals, which ranged from 250-1000 μ m in length and from 10-20 μ m wide. Some of these crystals are shown in Figure 3.26. Because of their inconsistent size, all possible sources of contamination were checked in order to see if the supposed crystals were fibres of something else. No similarly shaped fibres could be found from any source, either glass or cellulose and so it would seem that these really were crystals which had been produced during the synthesis. XRPD analysis of the bulk products in which the crystals were found showed them to be pure VPI-5, thus increasing the possibility that the needles really were exceptionally large crystals of VPI-5. Attempts were made to determine whether the huge crystals were single by viewing them through a microscope fitted with cross-polars: this was difficult to do because the microscope had a low magnification. The crystals did not seem to show an immediate extinction when viewed through cross-polars indicating that they may not have been single. Despite this two of them were mounted onto glass fibres in order to try and perform a crystal diffraction study. Attempts to carry out this study at Edinburgh did not succeed, due to the small size of the crystals, and unfortunately the delicate mounts broke before the crystals could be sent away for a further attempt on more sophisticated apparatus.

Figure 3.25 Crystals from a seeded solution of APHE which contained 60% PEG

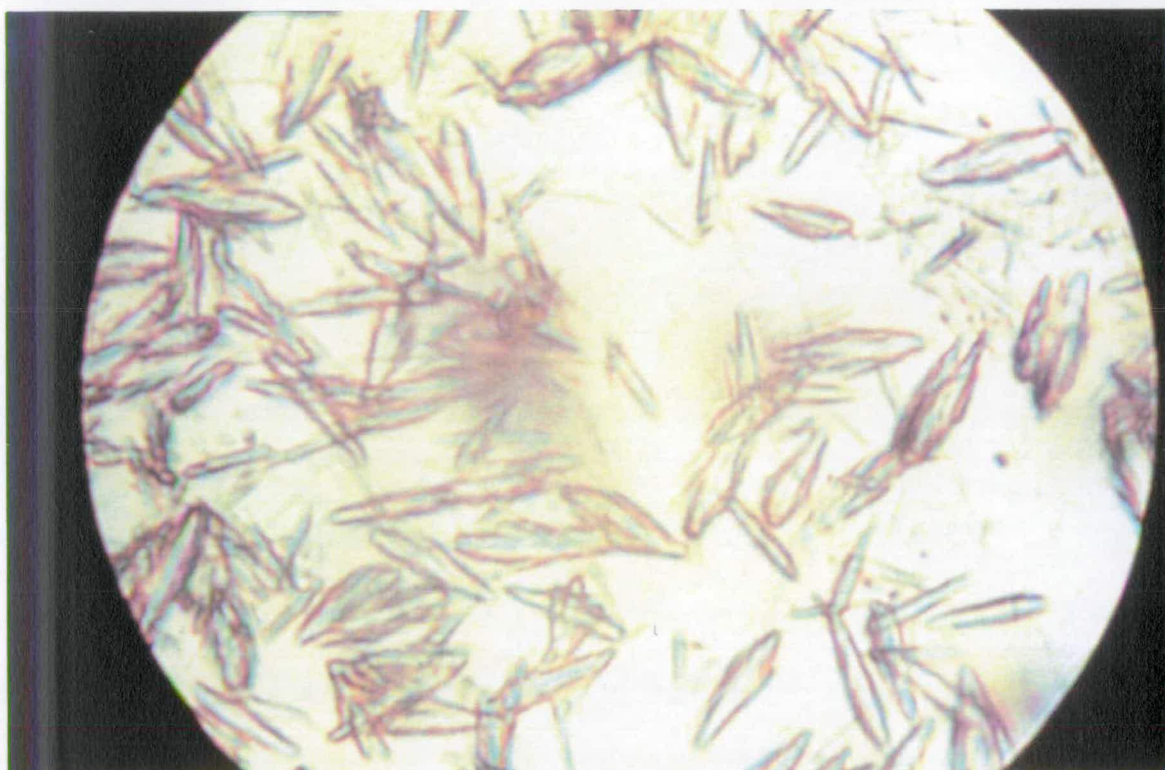
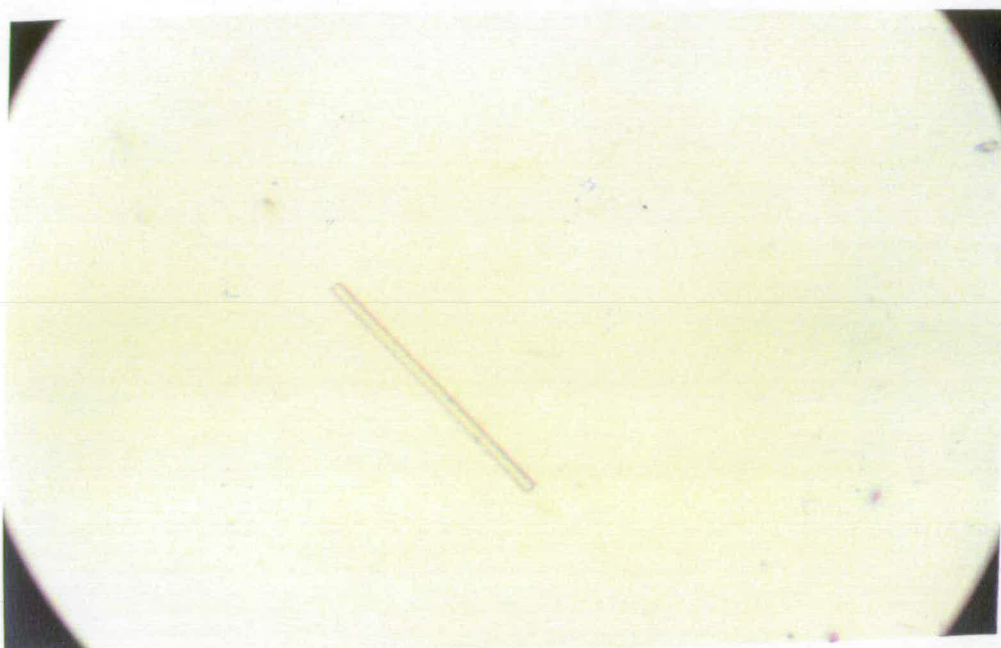
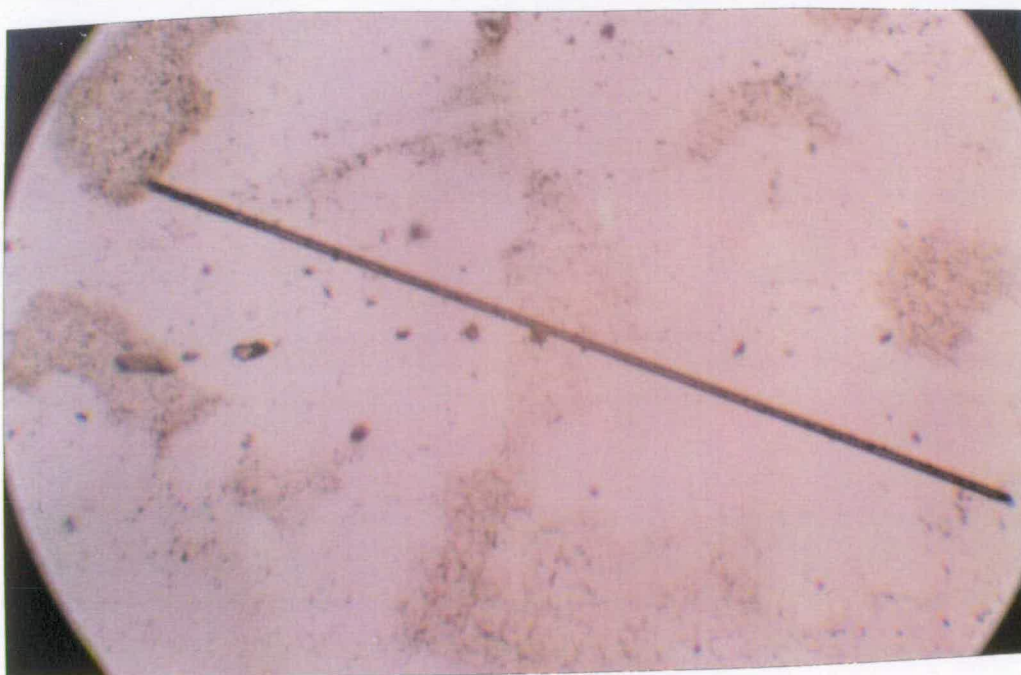


Figure 3.26 Apparent single crystals of APHE-VPI-5.



Crystal is 250 μm long.



Crystal is 1000 μm long.

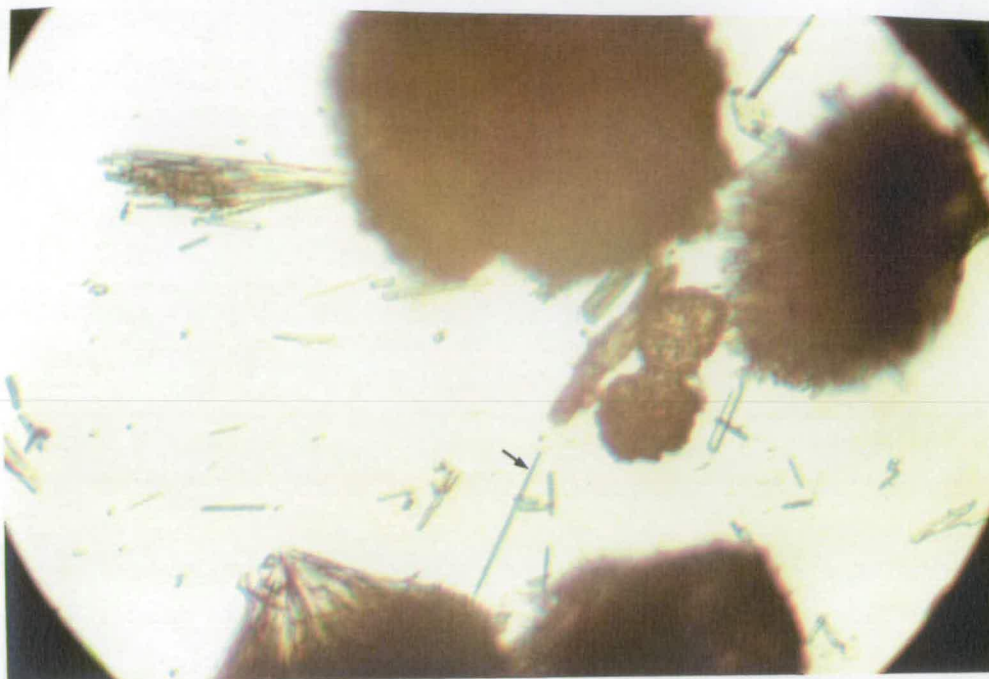
3.6 Were DPA- and APHE-VPI-5 the same material?

Both of the successful synthesis routes which have been described in this chapter were described as producing VPI-5, but was this really the case, or were two similar, but distinct phases produced? As was mentioned in the introduction to section 3.4 there has been discussion as to whether the material crystallised from an inorganic system should be described as VPI-5 or H1. The argument impinges upon this project because if they are different phases then the material which was synthesised from APHE would surely be more akin to H1 than to VPI-5. In the following discussion however, all phases synthesised in this project shall be referred to as VPI-5, but it will be made clear which route was used to synthesise them. The initial indications were that the two phases were the same material, and the reasons for this were:

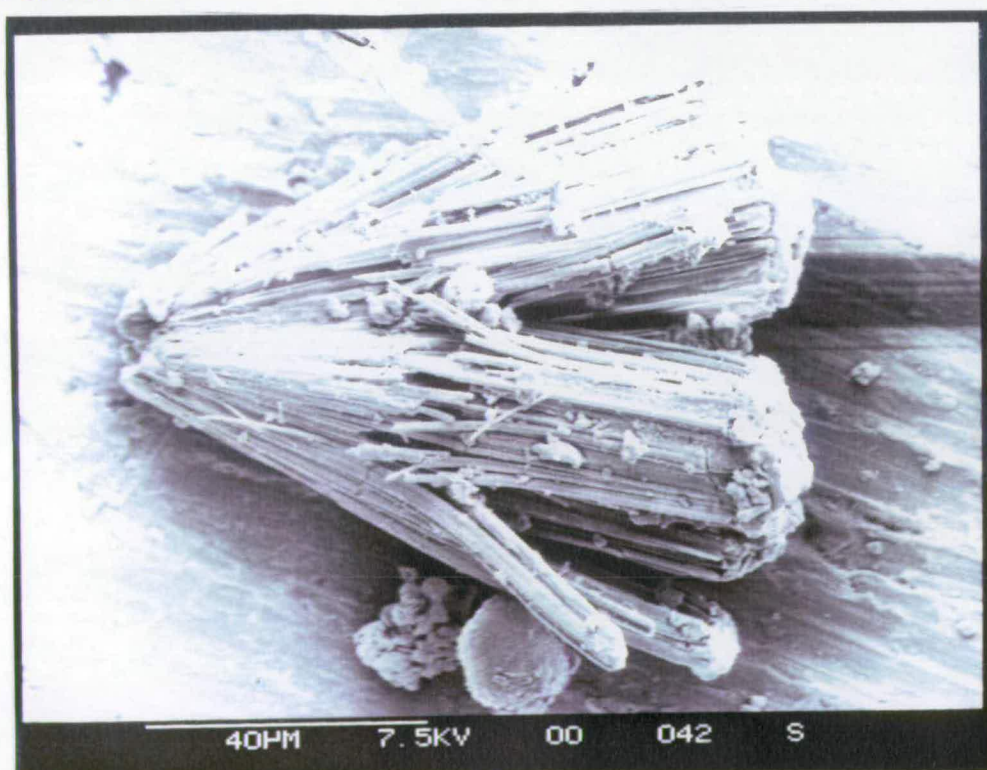
i) Their XRPD patterns were virtually identical, all the same peaks were present, even doublets. The only difference between the patterns was the relative peak intensities and, as was stated earlier, it is believed that these were due to preferred orientation effects with APHE derived VPI-5. The reason for this is that the needles could not be successfully ground to a powder and so lay on their long axis in the powder diffraction sample holder.

ii) Most physical differences between the differently synthesised VPI-5 samples were not as great as it seemed at first. VPI-5 synthesised in the presence of DPA occurred mainly in the form of wheatsheaves, but as Figure 3.27 shows, single needles also formed occasionally. It has already been described how APHE derived VPI-5 was seen to form wheatsheaf structures also, in addition to single crystals. One large difference which was discovered was in the Al/P ratios of the different types of VPI-5. Elemental analysis of the products was carried out by inductively coupled plasma atomic adsorption spectroscopy. This showed DPA-VPI-5 to have an Al/P ratio of 1.15, whilst APHE-VPI-5 had a ratio of 0.99. If both samples had perfect VPI-5 frameworks, the ratios would be expected to be 1:1. The ratio observed for DPA-VPI-5 is consistent with what others have seen [4, 9] and the phase has been identified by most authors as VPI-5, but a version which contains many framework defects. Thus the case for APHE-VPI-5 being the same phase as DPA-VPI-5 is not weakened by the difference in Al/P ratios, rather it suggests that the APHE route may produce a better VPI-5; yet another advantage for the new synthetic method.

Figure 3.27 Needles of DPA-VPI-5.



Needles of DPA-VPI-5 viewed under an optical microscope. The needle at lower centre is approximately 100 μm long. Note also the fibrous appearance of the part wheatsheaf.



Electron micrograph of part of a DPA-VPI-5 wheatsheaf showing fibrous bundles.

Further work reinforced the impression that both reactions had produced the same material, following chapters will describe how both types of VPI-5 thermally transformed to $\text{AlPO}_4\text{-8}$ and how both were seen to be capable of the sorption of large dye molecules. More detailed work was carried out to investigate the actual structures themselves, this consisted of ^{27}Al and ^{31}P solid-state nmr.

NMR

MAS NMR was carried out on samples synthesised by the two different routes. The samples were hydrated over a saturated salt solution in a closed vessel for 48 hours prior to analysis and all experiments were carried out at ambient temperatures of 293 - 296K. The conditions which were used to acquire spectra were equivalent to the conditions described by He *et al* [31].

^{31}P : Single pulse excitation spectra, as shown in Figure 3.28, were very similar to each other and also to the spectra reported for VPI-5 at ambient temperatures by others [31, 32, 33, 34]. They show three resonances, at δ -23, -27 and -33ppm, with 1:1:1 ratios. The first two have been assigned to 6-4 sites made crystallographically inequivalent due to distortion of the framework by octahedral aluminium, whilst the resonance at -33ppm is assigned to the 4-4 site.

Cross-polarisation spectra (see Figure 3.29) were not as similar, there was an extra resonance for each sample, but they were at quite different positions:

-13.8ppm for DPA-VPI-5

-17.4ppm for APHE-VPI-5

Davis *et al* [32] saw a similar peak at -16.3ppm for a sample of VPI-5 which had been synthesised with TBAOH as the structure directing agent. They assigned the peak to P-OH sites and speculated that the sites occurred in a number of different environments such as on the surface and at internal defects. Kolodziejewski *et al* [34] also assigned a peak in this area to P-OH when working with DPA-VPI-5. Although they did not state an exact position for their resonance, it appeared from their published spectrum to be shifted towards a higher frequency than -15ppm, i.e. towards -14ppm.

Evidence from this work and the referenced work suggests that if all of the peaks seen in the -13 to -18 ppm range are due to P-OH then their variable positions are probably due to different Al / P ratios in the different samples, as follows:

- DPA-VPI-5 has the lowest Al / P ratio and its P-OH peaks occur between the frequencies of -13.8 and -15ppm.
- TBAOH-VPI-5 has been claimed (B13) to have an Al / P ratio of nearly 1 and its resonance occurred at -16.3ppm.
- APHE-VPI-5, with a P-OH resonance at -17.4ppm has an Al / P ratio of very slightly under 1.

²⁷Al: Single pulse excitation spectra were acquired and are shown in Figure 3.30. They agree very well with the spectra obtained by others [31, 35], including the lineshapes of the resonances at -20ppm, which are due to octahedrally co-ordinated aluminium. What can also be seen, however, is that the DPA-VPI-5 has a low intensity resonance at about 5ppm, which is not seen on the spectrum of APHE-VPI-5. Although it is only just noticeable, the spectra of He *et al* [31] also show this resonance, which they attributed to 5-coordinate Al atoms formed by the detachment of water from 6-coordinate aluminium. This seems unlikely to be the sole cause because, although the line was more noticeable in their spectra of partially dehydrated VPI-5, it was definitely present in the fully hydrated spectra. Also, care was taken in this work to ensure that the DPA-VPI-5 was fully hydrated prior to nmr analysis, yet the line still showed.

Wu *et al* [36] showed spectra of VPI-5 at a range of hydrations and did not see a resonance at 5ppm, but did see a complicated set of resonances around 20 - 40ppm, one of which (22.8ppm) they assigned to 5-coordinate Al formed by partial dehydration of Al(VI). However, the same authors later [37] see a resonance at about approximately 7ppm in the ²⁷Al spectrum of hydrated AlPO₄-5 and ascribe that too to 5-coordinate Al, stating that this is due to an aluminium microstructure which is not well ordered.

So what caused the resonance in VPI-5? It seems likely that it did arise from 5-coordinate Al, but probably not through dehydration. Instead 5-coordinate Al may be due to either the absence of P atoms from the framework, or it may be that small amounts of n-dipropylamine present in the channels prevent some aluminium atoms from co-ordinating to two water molecules.

In summary, the differences which have been seen between the two materials are consistent with their having the same basic structure, but with the DPA-VPI-5 having a more disordered framework due to missing P atoms. Thus APHE-VPI-5 is more akin to the classic VPI-5 framework structure in that it has an Al / P ratio of nearly 1, although it lacks the exact crystal morphology usually associated with VPI-5.

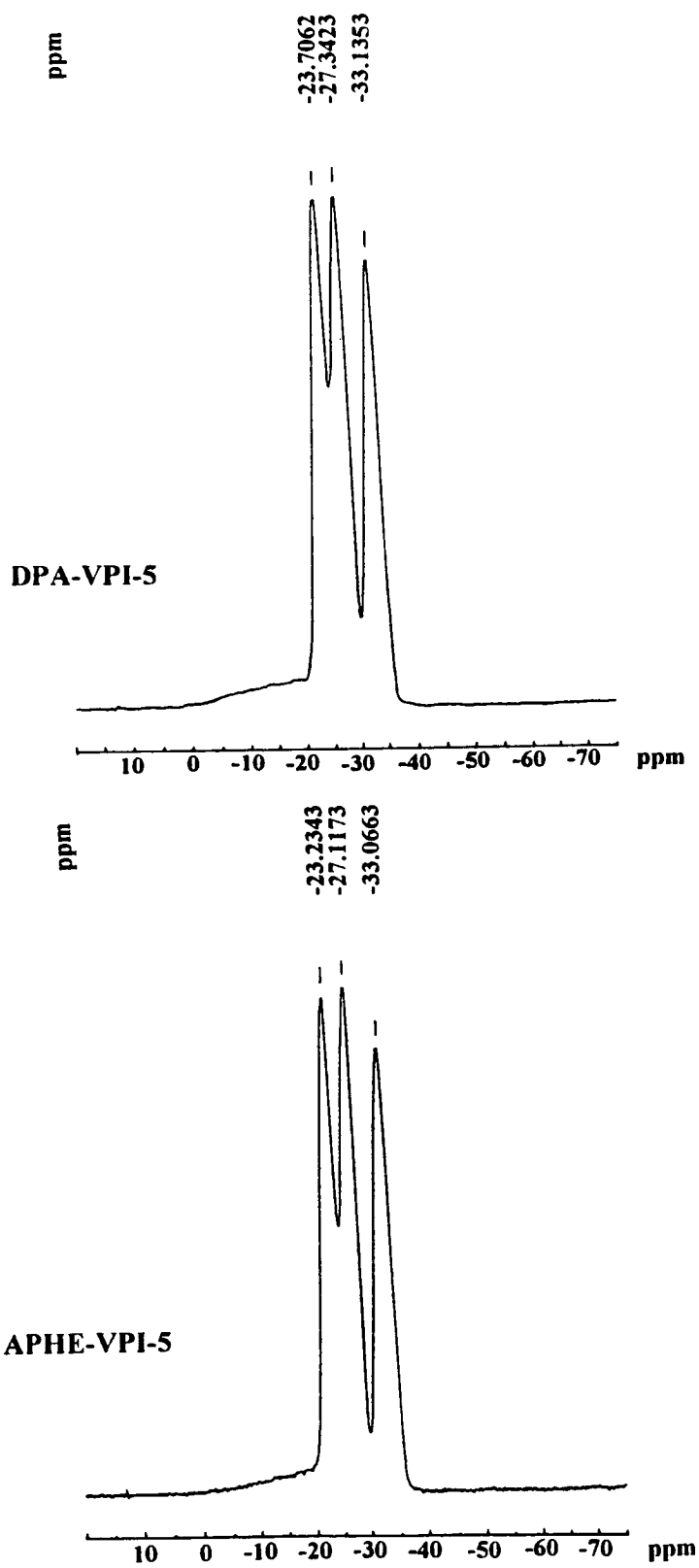
Figure 3.28 ^{31}P masnmr of VPI-5

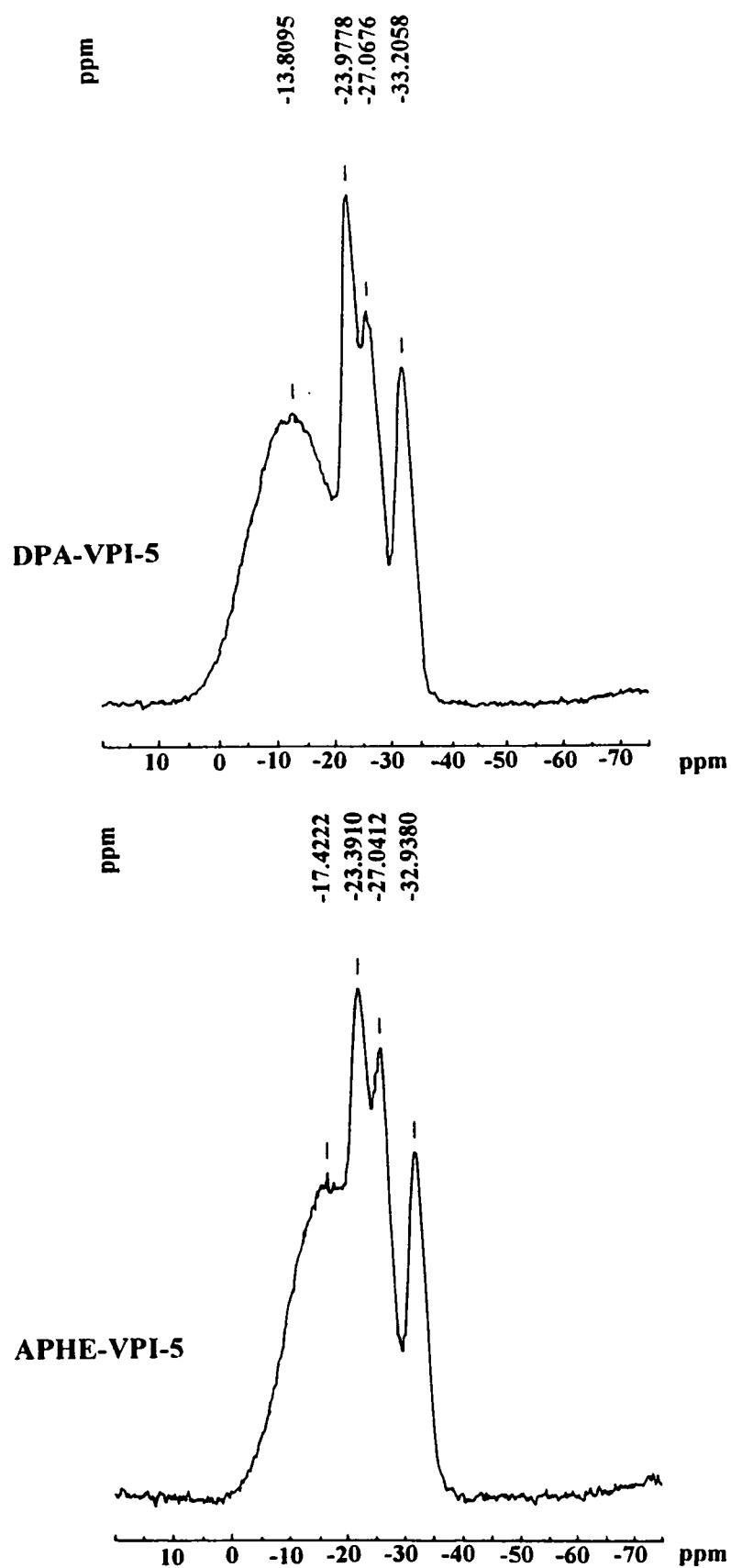
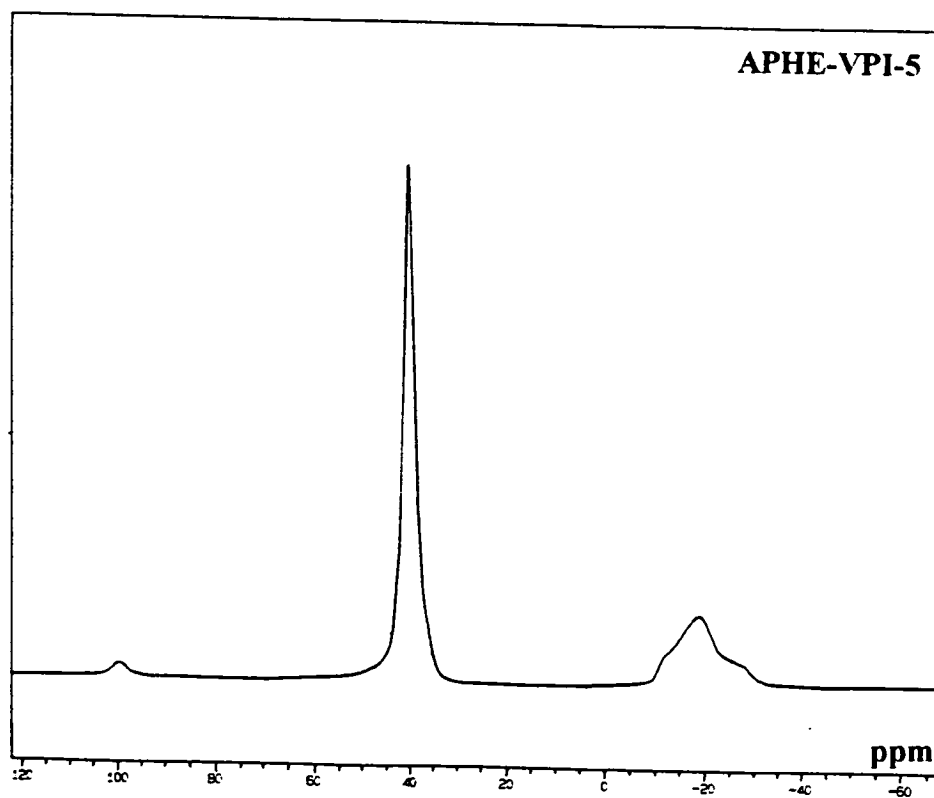
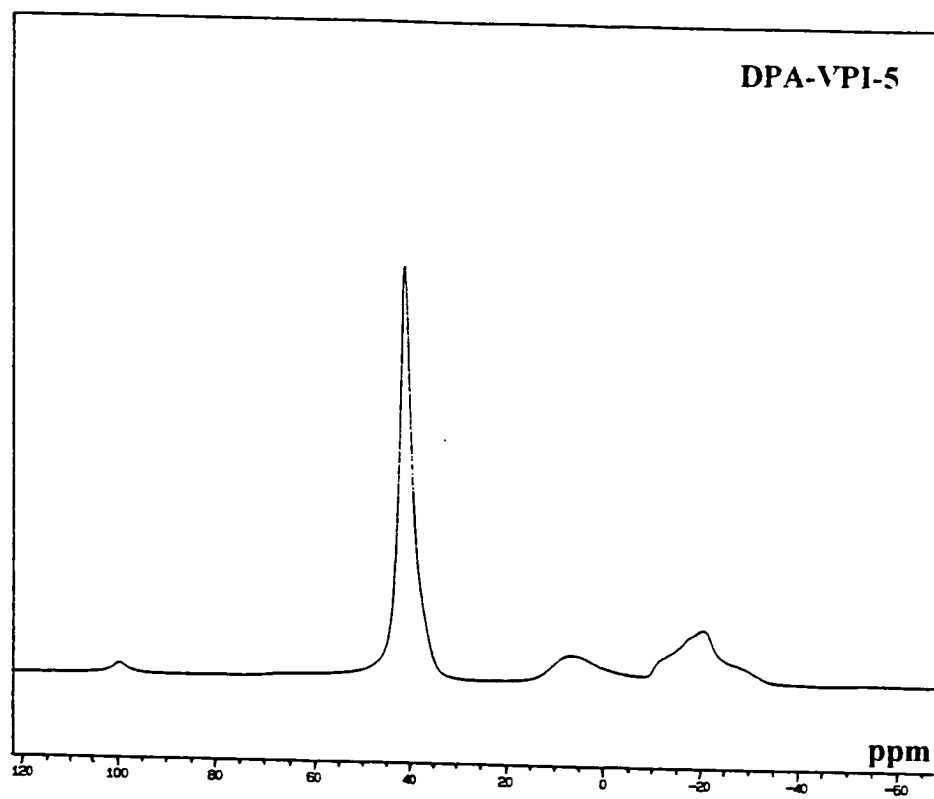
Figure 3.29 Cross-polarised ^{31}P masnmr of VPI-5

Figure 3.30 ^{27}Al masnmr of VPI-5

3.7 Discussion of the H1 / VPI-5 Question.

It seems highly probable that both of the synthesis routes used in this project produced VPI-5, even though one of them was a more or less inorganic system, so does that mean that a repeat synthesis of H1 has still not been achieved?

H1 was an aluminophosphate first reported in 1962 by D'Yvoire [16], which he prepared by precipitation from a solution of Al_2O_3 and phosphoric acid. A series of hydrated aluminophosphates were prepared, which he labelled H1 to H3. None was ever synthesised as a pure phase, they always formed as mixtures along with variscite and metavariscite. H1, in particular was only ever formed in small quantities, mixed with larger quantities of H2 and H3. D'Yvoire reported that when the compounds were heated, they transformed to AlPO_4 -tridymite. Soon after the synthesis of VPI-5 was reported, it was noted that there was a similarity [38] between its XRPD pattern and that of H1. However several peaks were present in the VPI-5 pattern which were missing from the reported H1 pattern and so it was claimed that this showed the two phases to be different.

Various workers have attempted to repeat the work of D'Yvoire in the hope of producing a pure sample of H1, so that the argument could be settled, however no successes have been reported. The closest reported synthesis was that of Duncan *et al* [20, 39], who carried out an "organic free" synthesis, which produced a pure phase containing all the peaks of VPI-5 and which, they claim, shows that VPI-5 and H1 are the same since, by variation of heating and composition, H2 and H3 were also produced. Davis *et al* [4] claimed that this material was VPI-5 since all of the VPI-5 peaks were present, but was not H1. Without a pure sample of H1, prepared with exactly the technique that D'Yvoire used, it is impossible to say with certainty whether or not H1 and VPI-5 are the same or different, however it is believed that a case can be put for saying that H1 and VPI-5 are the same material.

The argument against the missing peaks showing there to be a difference between the two phases is that, since H1 never comprised more than 15% of any sample, the missing peaks may be due to overlap with stronger H2 peaks [16]. Davis *et al* dispute this on the grounds that there are VPI-5 peaks which d'Yvoire did not report and which do not overlap with any H2 peaks. However, the intensities of the missing peaks which do not overlap are low [4] and they could possibly have been too weak to see if there was only a maximum of 15% VPI-5 in the sample. This argument is supported by the XRPD patterns detailed earlier in this chapter in which not only are

several prominent $\text{AlPO}_4\text{-11}$ peaks hidden by VPI-5 peaks in samples which contained more than 25% $\text{AlPO}_4\text{-11}$, but also some smaller peaks were not seen which should not have overlapped with any VPI-5 peaks, e.g. those at d spacings of 3.13 and 3.36, which have I/I_0 values of 19 and 21 respectively.

The synthesis route which was reported by Duncan *et al* [39] also produced the aluminophosphates H2 - H4, and variscite and metavariscite, i.e. all of the other phases which D'Yvoire had synthesised, with no exceptions and no extras. This strengthens the case that H1 and VPI-5 are the same thing, for it seems strange that it should be possible to synthesise every member of the series except H1, and instead synthesise a totally new member, viz. VPI-5. The discovery [39, 40, 41] that variscite, metavariscite, H2 and H3, the other members of the series whose structures are known, all contain octahedral aluminium sites, just as VPI-5 does, suggests that they may share similar basic building units, in which case D'Yvoire's synthesis would have been able to produce VPI-5 alongside the others. Certainly it has been shown that H2 and VPI-5 are constructed from the same hydrated chain building unit [42]. This is very strong circumstantial evidence that VPI-5 and H1 are the same material.

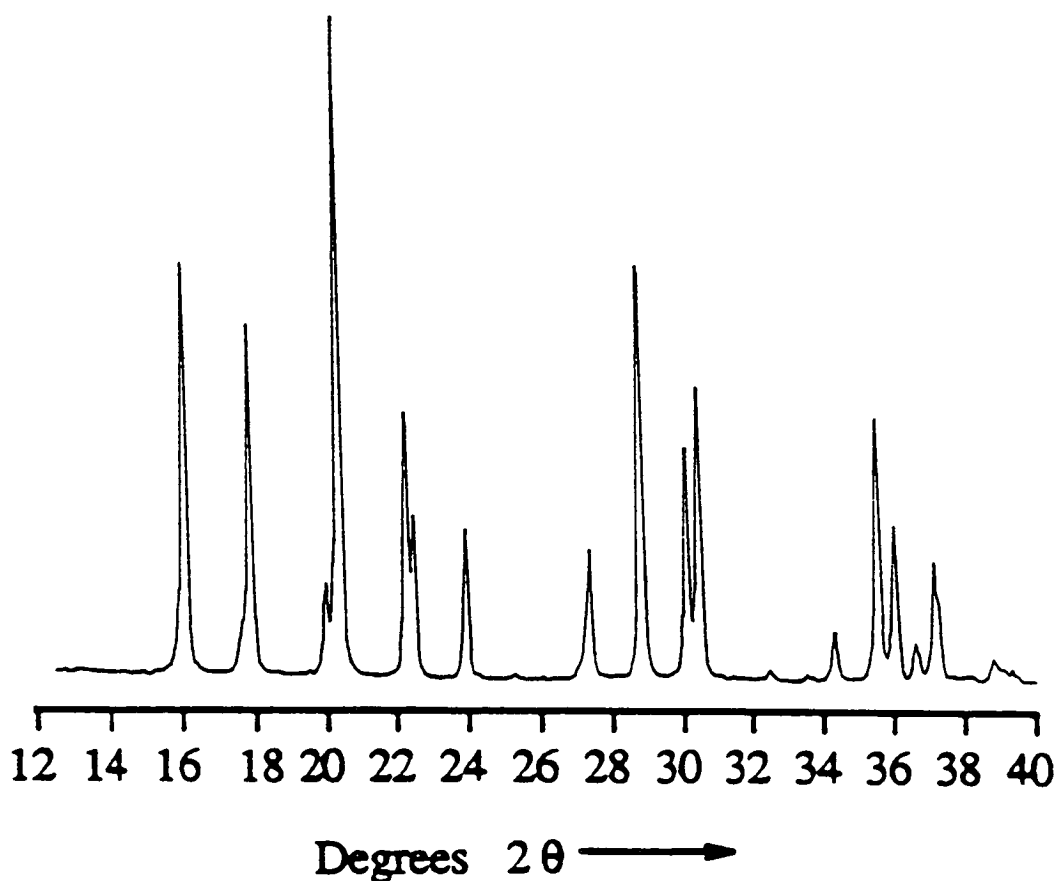
Another piece of evidence used to support the claim that VPI-5 and H1 were different was the fact that VPI-5, when heated, transforms to $\text{AlPO}_4\text{-8}$, whilst H1 was said to transform to $\text{AlPO}_4\text{-tridymite}$ [11]. Again the explanation may lie with the fact that there was only a small quantity of H1 present in the products, so that the peaks of any $\text{AlPO}_4\text{-8}$ formed through thermal transformation of H1 could have been overshadowed by much stronger $\text{AlPO}_4\text{-tridymite}$ peaks, which are known to form from heated H2 and H3. Szostak claimed [43], although this was later thought doubtful, that the reason for D'Yvoire's success, and the failure of others to repeat his work, was because his alumina source was contaminated with HCl. If this was the case, and the H1 containing sample had not been thoroughly washed, then low temperature formation of $\text{AlPO}_4\text{-tridymite}$ could have happened very easily. Such a transformation was seen in this project, in a sample of VPI-5 prepared from APHE.

Finally, there is the question of morphology. It seems very likely that the two phases prepared in this project were both VPI-5 and yet there were differences in their morphologies, albeit ones which could be reconciled. D'Yvoire's description of the morphology of H1 is as follows: "Fine needles ... , often grouped in bundles showing little divergence." [16]. This description fits much of the product produced by the APHE route, which is the one which is closest to that of D'Yvoire, and so adds its weight to the evidence that VPI-5 and H1 are the same material.

3.8 Synthesis of a Gallium Phosphate Precursor

APHE is a member of a family of soluble phosphates which also includes iron, titanium and chromium versions [44]. Attempts were made here to also synthesise a gallium version (GPHE). The reason for this was that a gallium containing analogue of VPI-5 might be catalytically active. Synthesis followed exactly the same procedure as APHE synthesis, with gallium chloride replacing aluminium chloride, however no solid precipitated from the solution. The sides of the vessel were scratched and the solution cooled over a 60/80 pet.ether slush to just above the point where the solution froze. Still no precipitate was observed. Solvent was evaporated, under mild conditions, by use of a rotary evaporator to try and force a precipitate. This did produce a white solid, however XRPD analysis indicated that this was most probably a gallophosphate analogue of variscite, Figure 3.31 shows the XRPD pattern.

Figure 3.31 GaPO Variscite.



The solutions were investigated by P-nmr on a Jeol FX90Q at 36.56 MHz and the results compared to those obtained from P-nmr analysis of APHE solutions, to see if this would supply clues as to what was happening. Spectra were referenced to orthophosphoric acid (85% in water) in ethanol.

The solution of gallium chloride and phosphoric acid showed only one sharp peak, which was the same as that generated by the reference. In contrast very different peaks were seen in the series of spectra which involved APHE. The nmr spectrum recorded from the supernatant liquid left above precipitated APHE had two main peaks, a large one at -14.7ppm (with a shoulder at 17.8ppm) and a smaller one at -24.8ppm.

When APHE was dissolved in dry ethanol and analysed, it gave only the peaks at around 24.8ppm. It should be noted that very little APHE dissolved in dry ethanol. After standing for two weeks, this sample was reanalysed and now found to have peaks at 14.8 and 17.9ppm. It seemed probable that the new peaks belonged to APHE whose framework had been hydrolysed. Another spectrum was recorded for a solution of APHE in wet ethanol, that is ordinary lab grade ethanol. The APHE dissolved readily in this and peaks were around 14-18ppm, which suggested that peaks in this region really were attributable to hydrolysed APHE.

From all of this evidence it seems likely that no gallium equivalent of APHE had been formed whatsoever. If soluble GPHE had formed then a change would have been expected in the P-nmr spectrum of the solution, however no such change was seen.

Further attempts were made to incorporate gallium into an APHE-type structure by making mixed solutions of gallium and aluminium chlorides prior to H_3PO_4 addition. None of these gave a product and so it is concluded that it is not possible to incorporate gallium into APHE.

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Chapter 4

The Stability of VPI-5

4.1 Introduction

All molecular sieves are metastable phases [1], although some undergo transition much more easily than others. It now seems that VPI-5 fits into the category of those that easily undergo transition. When VPI-5 was first reported [2] there was great excitement about the potential uses of its extra-large pores. It was initially claimed that the structure was thermally stable, as its XRPD pattern remained substantially the same after heating to 800°C [3]. However, the XRPD patterns were not shown and details of the heating conditions were not given. It will be seen later that the lack of these two results prevents a proper assessment of the results.

As interest in VPI-5 grew, it was found that, unlike most other AlPO_4 s, VPI-5 was thermally unstable and, as was outlined in Chapter 1, transformed partially or wholly to the structurally related molecular sieve AlPO_4 -8 when heated. This transformation was itself the subject of much investigation for it seemed that the rate and extent of the process varied greatly and was dependant upon several factors. A clue was the discovery [4] that VPI-5 was an aluminophosphate hydrate, in which some of the water molecules were actually bound to the framework rather than just sorbed into the pores as in most molecular sieves. At first it was thought [5] that the transformation was reversible in some samples and that it was the presence of crystalline impurities which stopped others from being reversible. These crystalline impurities were also suggested as the reason why samples of AlPO_4 -8 showed such low pore volumes. Pore blockage was soon, however, found to be due to stacking faults which formed during the transformation to AlPO_4 -8 [6,7,8]. As can be seen in Figure 4.1, this is because the conversion can take place in any of three directions. Thus Sorby *et al* [6] found that as little as 10% transformation led to as much as 80% loss of adsorption capacity and Martens *et al* [7] demonstrated that dehydrated VPI-5 which appeared pure by XRPD had enough AlPO_4 -8 formed at the outsides of the

crystals for the pore entrances to be narrowed. From such a situation it would be difficult for VPI-5 to reform, and the irreversibility of the change was widely suggested [9,10,11].

Figure 4.1 The transformation of VPI-5 into $\text{AlPO}_4\text{-8}$ can occur in three directions.

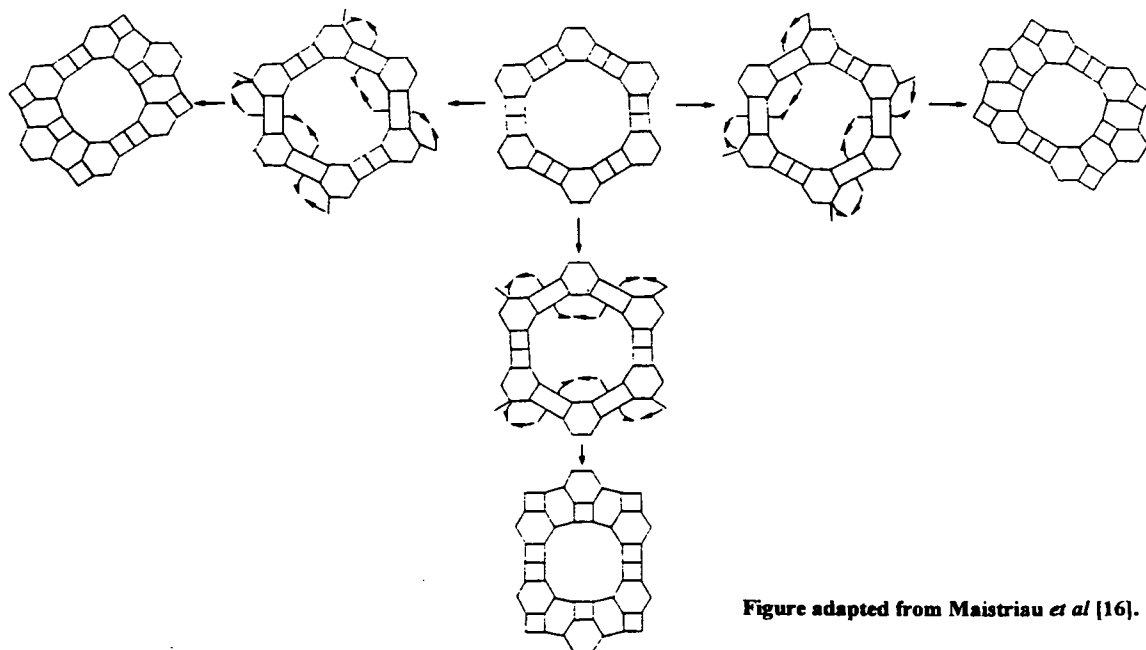


Figure adapted from Maistriau *et al* [16].

A way was found in which VPI-5 definitely could be heated without loss of structure [10]. That way was to first dehydrate the VPI-5 at room temperature and under a strong vacuum (10^{-5} Torr). After that it could be heated and cooled many times without effect and could even be exposed to steam at temperatures above 550°C without loss of structure, just so long as the VPI-5 remained dehydrated whilst being raised to 550°C .

This strongly suggested that $\text{AlPO}_4\text{-8}$ formation involved hydrolysis which was prevented by removal of water prior to heating, at a temperature too low to activate the transformation. The same paper made several other points of note: It reported that if VPI-5 was heated in ambient air, then rapid heating ($20^\circ\text{C min}^{-1}$) was preferable to slow heating (1°C min^{-1}), as the former led to only a small amount of $\text{AlPO}_4\text{-8}$ formation whilst the latter caused near complete transformation.

Also in that paper came a suggestion as to why VPI-5 synthesised with different organics showed different stabilities. It was that some routes produced more structural defects and these assisted or possibly initiated the hydrolytic transformation.

For example the least stable form of VPI-5, that synthesised with di-n-propylamine, was shown [12] not to have an Al/P ratio of 1 and also to have many hydroxyl groups, therefore it probably has many defects, whilst the relatively more stable form which is synthesised with tetrabutylamine hydroxide did have an Al/P ratio of 1. As will be seen, these hydroxyl defects are thought to make transformation to $\text{AlPO}_4\text{-8}$ easier. Even with the stable forms of VPI-5, however, heating has generally produced some degree of conversion to $\text{AlPO}_4\text{-8}$.

It was also suggested [10] that if as-synthesised product was thoroughly washed the stability was increased, for all methods of synthesis. The suggested wash was to slurry the product in boiling water for several hours and recover by filtration. For well crystallised samples, it was claimed that this gave a product which gave only small amounts of $\text{AlPO}_4\text{-8}$ if heated at 100°C for 4 days. The reason given [13] was that washing removed impurities which aided transformation. Further work [14] confirmed that washing led to improved stability and suggested that as well as the removal of impurity, washing caused the formation of a better ordered triple helix of water in the channels. The presence of the triple helix had been recently reported [15] ~~and is shown in Chapter 1.~~ It was suggested by Potvin *et al* that the framework water could be stabilised by a more ordered triple helix. This, they argued, could help to stabilise the framework because they thought that structural water in turn helped to stabilise the framework, hence its removal could lead to $\text{AlPO}_4\text{-8}$ formation. It subsequently turned out that structural water did indeed help to stabilise the framework [16]. VPI-5 was also washed with ethanol [12], but without any apparent gain in stability.

The minimum temperature at which transformation could begin remained unclear for a long time. Even after Martens *et al* [7] claimed that $\text{AlPO}_4\text{-8}$ could form, albeit very slowly, if VPI-5 was dehydrated at room temperature, few claimed that the process could occur even as low as 70°C [17,18] whilst most papers which gave a temperature for initiation still claimed it to be around 100°C [8, 19,20].

It was against this background of changing and sometimes conflicting data that much of this work was done, some of it to try and clarify the situation, and thus some work which will be described in this thesis was similar to that just mentioned as it was done concurrently.

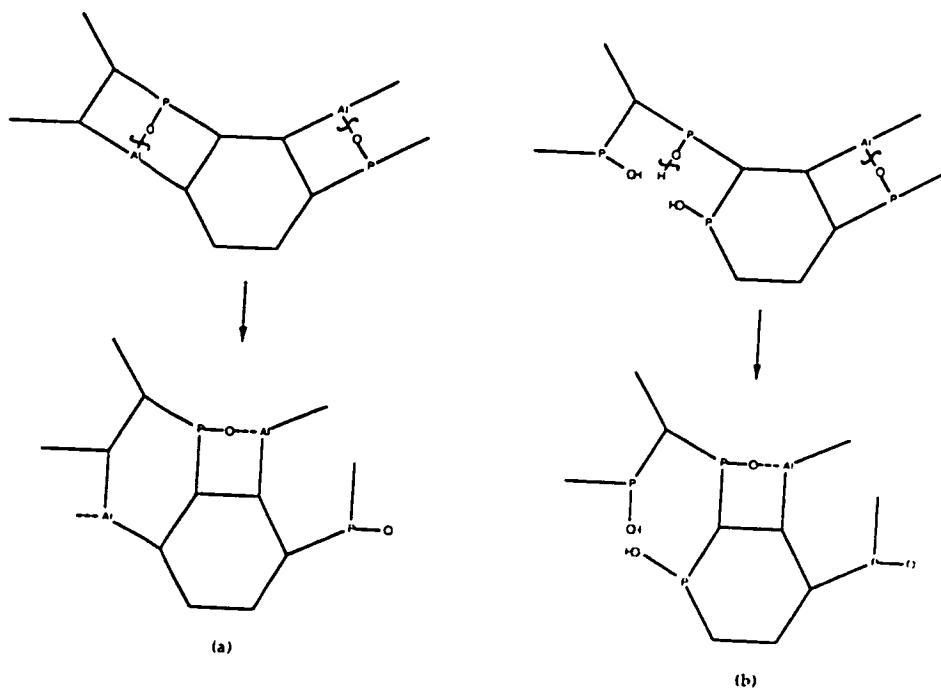
From all of the work described, there had emerged a fairly clear view of what affected the thermal stability of VPI-5 and it probably useful to give a short summary. VPI-5 usually transformed wholly or partially to $\text{AlPO}_4\text{-8}$ when it lost its structural water,

the exception being when dehydration occurred at low temperature and strong vacuum. The transformation was irreversible and started at the outside of crystals so that even if there was only slight transformation there was a large loss in adsorption capacity [8].

"The extent of the transformation depends on the rate of heating, the ambient atmosphere, the manner of sample washing, the kind and concentration of impurities, the nature of the organic template, and on the presence or otherwise of framework defects." [20].

The mechanism of transformation is shown in Figure 4.2 for both an ideal framework and a defect site.

Figure 4.2 The structural transformation of VPI-5 into $\text{AlPO}_4\text{-8}$ [20].



a) Defect-free VPI-5 transforms through a bond rearrangement which involves the breaking of two Al-O bonds.

b) A defect site transforms through a bond rearrangement in which one Al-O and one O-H bond are broken.

Two Al-O bonds need to be broken in the ideal framework, with an approximate energy of 120 kcal mol⁻¹ per bond, whilst for the defect site it is an Al-O bond at approximately 120 kcal mol⁻¹ and an O-H bond at approximately 100 kcal mol⁻¹ which need to be broken [20]. The lower energy requirement of the second case helps to explain why a defect-ridden structure such as DPA-VPI-5 is more unstable than structures with P:Al = 1.

It was suggested [21] that a driving force for this rearrangement to occur is the fact that the double 4-rings of VPI-5 are in trans-conformations. In almost all other molecular sieves in which there are double 4-rings, they occur in the more favourable cis-conformation. Unfavourable bond angles formed by trans-conformation are removed in VPI-5 by the six-coordinate Al-dihydrate site. However, once dehydration occurs, the trans-conformation becomes energetically unfavourable thus helping to drive the process of bond-rearrangement which leads to AlPO₄-8.

4.2 Stability of As-Synthesised VPI-5

An understanding of the thermal stability of VPI-5 was vitally important to this project because in order to force large organic molecules into the pores it was likely that elevated temperatures would be required. To this end the stability was thoroughly investigated under straightforward heating and also under other conditions likely to be encountered in attempts to load the material with organics, with an aim to find suitable temperatures which gave a trade-off between slow rate of transformation to AlPO₄-8 and high dye mobility.

4.2.1 DPA-synthesised VPI-5

Measurement of activation energy for the conversion of VPI-5 to AlPO₄-8

A large number of 10mg samples of VPI-5, synthesised via the DPA route, were heated at different temperatures for a range of times in order to produce data on the thermal stability of the material. Temperatures used were 65, 80, 95, and 110°C, the samples were spread thinly across the bases of 2ml glass vials in order to allow easy escape of water and so minimise any local areas of high water vapour concentration which could have affected stability (*vide ultra*). Figures 4.3-4.6 show XRPD patterns of the heated powders, which chart the transformation.

Figure 4.3 The effect of heating VPI-5 at 65°C

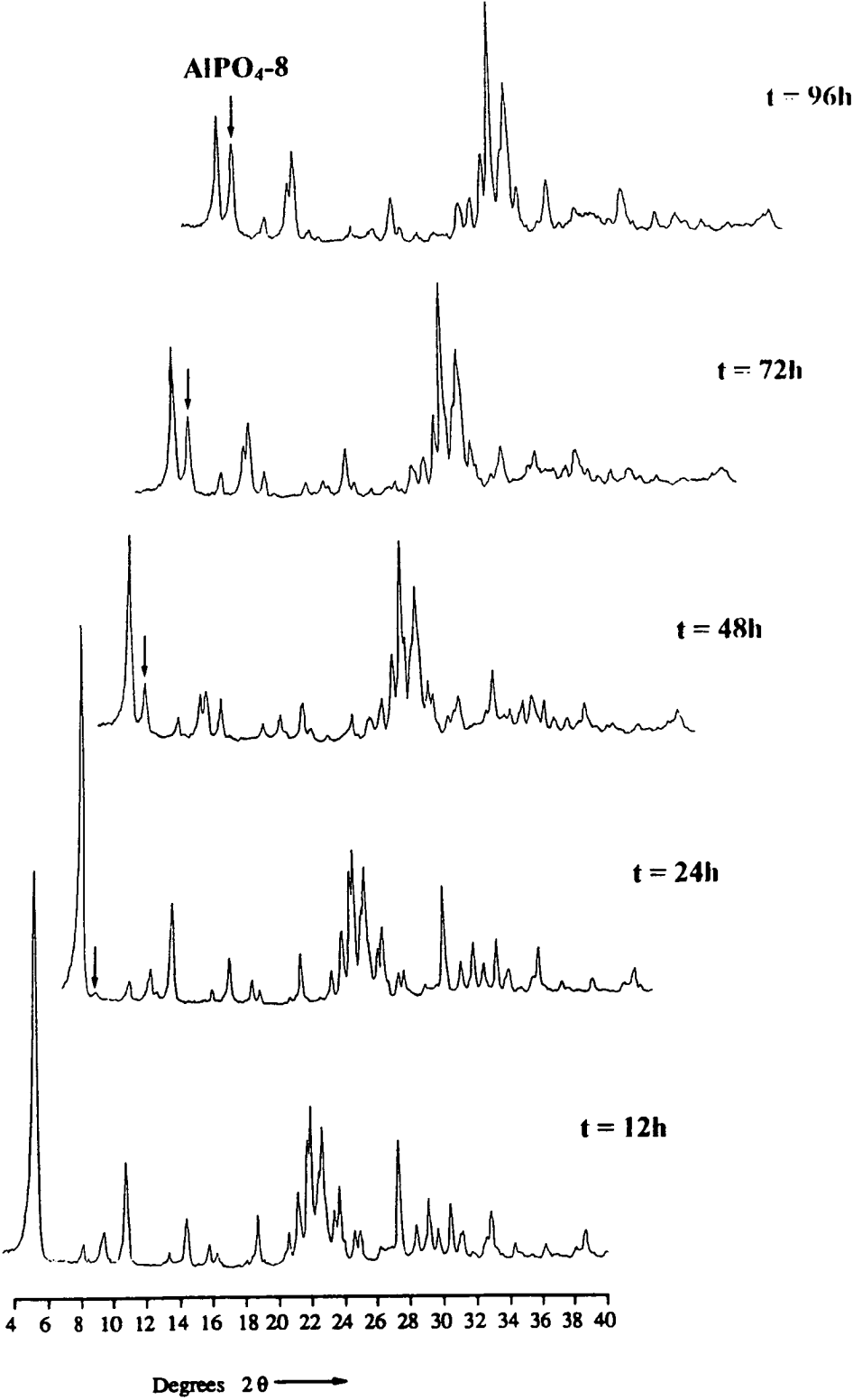


Figure 4.4 The effect of heating VPI-5 at 80°C

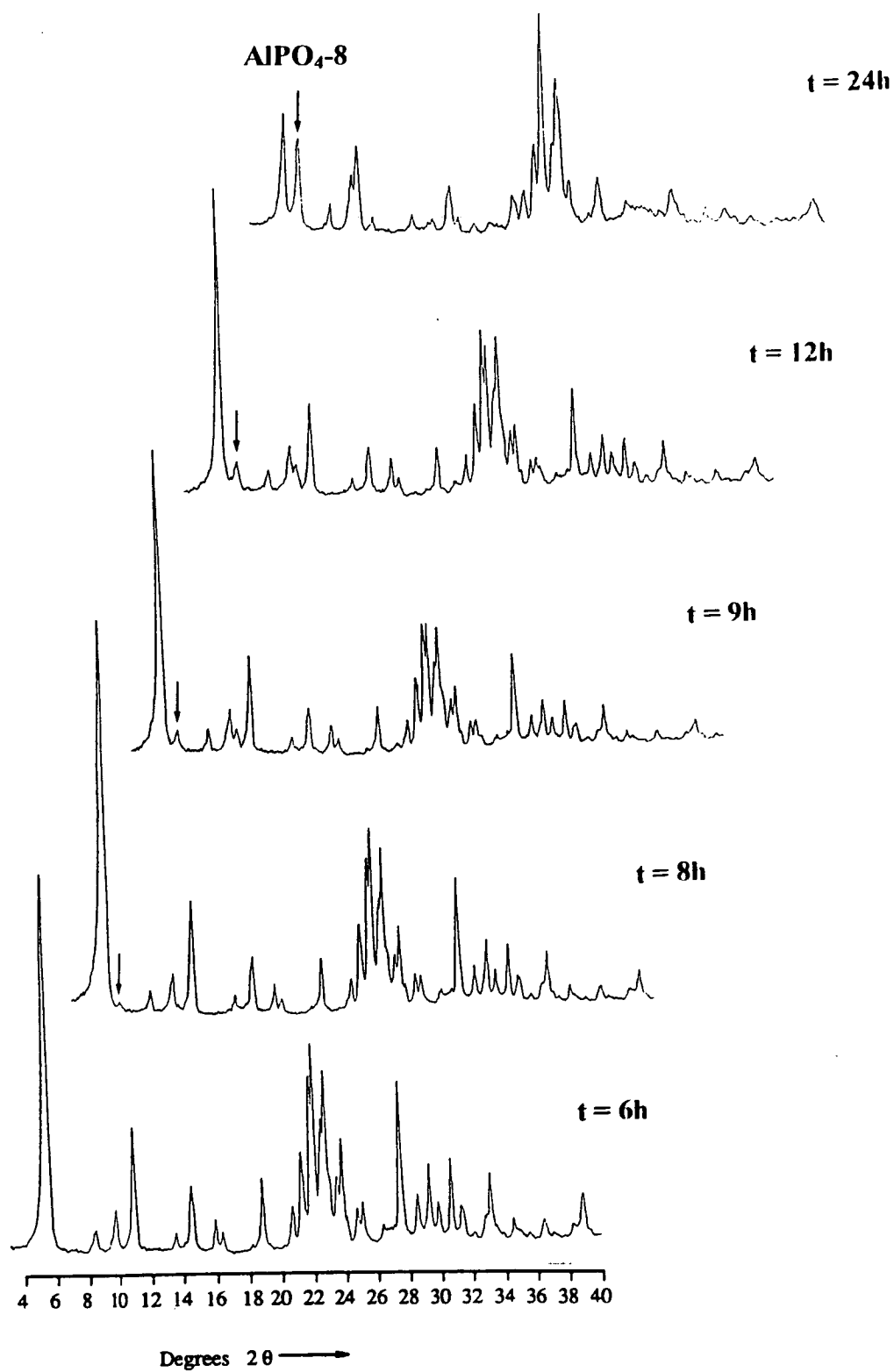


Figure 4.5 The effect of heating VPI-5 at 95°C

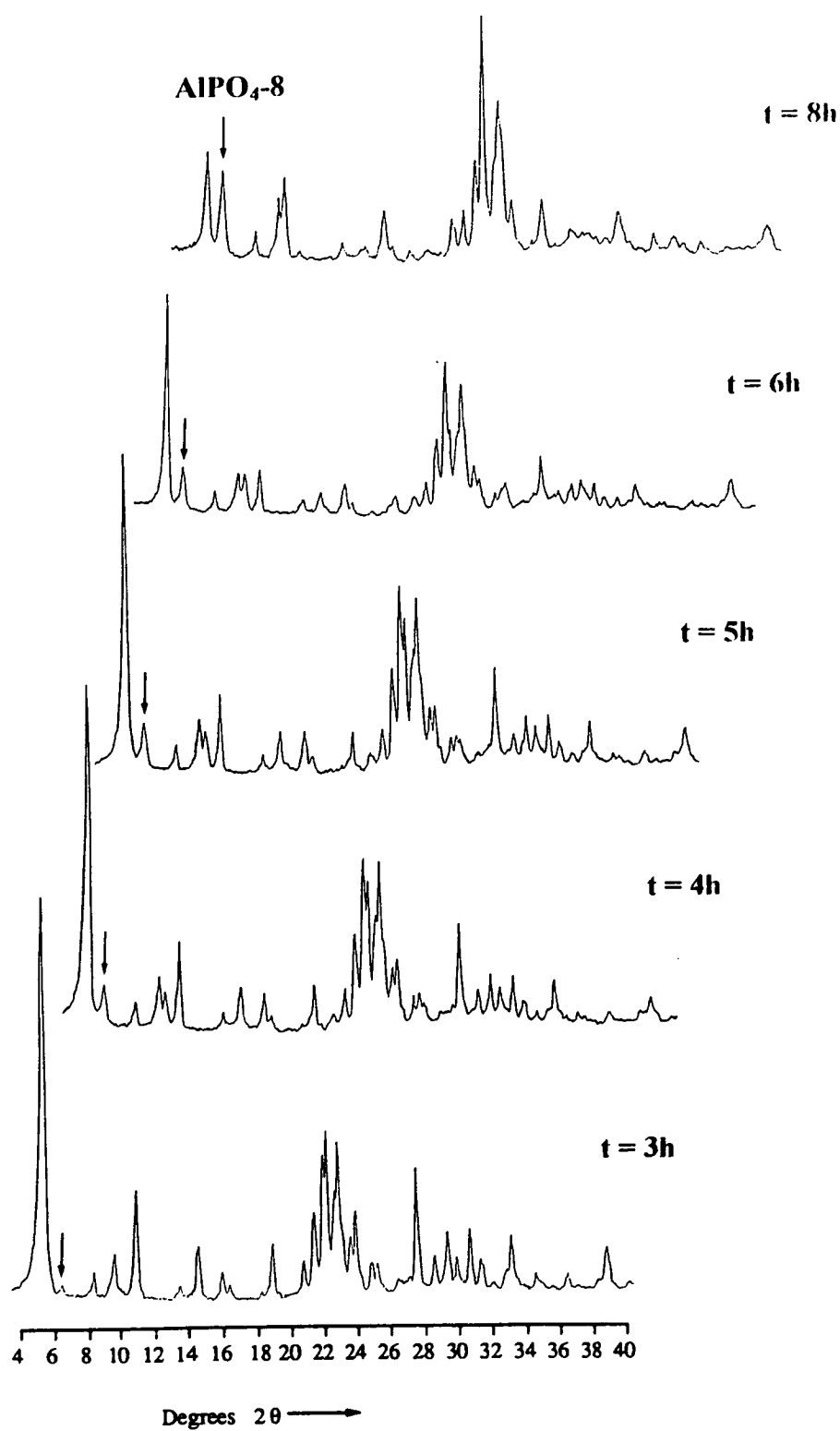
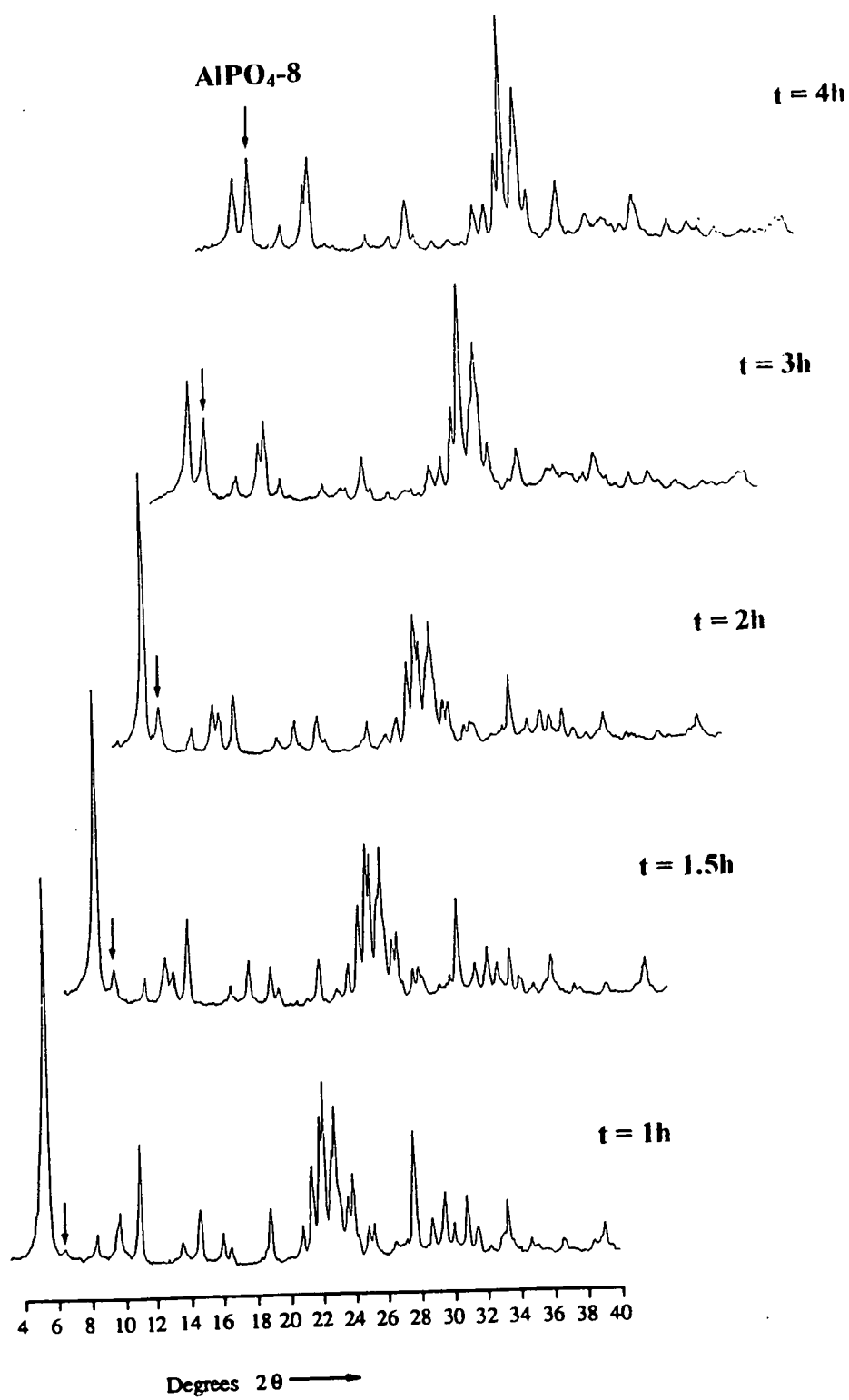


Figure 4.6 The effect of heating VPI-5 at 110°C



In order to quantify the degree of transformation from VPI-5 to $\text{AlPO}_4\text{-8}$ a calibration curve was required. This was constructed in a similar fashion to those of Chapter 3, with the aid of a set of standards which contained known quantities of VPI-5 and $\text{AlPO}_4\text{-8}$. Nearly pure DPA synthesised VPI-5 from the batch VS6 was used as the source of both VPI-5 and $\text{AlPO}_4\text{-8}$. In order to form $\text{AlPO}_4\text{-8}$, 0.5g of VS6 was heated at 80°C overnight, followed by rehydration and reheating until there was no sign of any VPI-5 remaining, as indicated by the loss of the peaks at $2\theta = 10.8$ and 18.8 .

The calibration curve was obtained like those in Chapter 3, by measurement, from XRPD patterns, of the heights of lines specific to each phase. The lines used were chosen because they were the most free from interference and were at:

$$2\theta = 10.8 \text{ and } 18.8 \text{ for VPI-5}$$

$$2\theta = 6.2 \text{ and } 9.9 \text{ for AlPO}_4\text{-8}$$

VPI-5 and $\text{AlPO}_4\text{-8}$ are hydrated to different degrees, this had to be taken into account when the calibration curves were made because the proportions of the two phases had to be measured relative to their AlPO_4 contents. Samples of each were equilibrated over saturated NaCl solution to constant relative humidity. Thermogravimetric analyses of the two phases were recorded, which showed the water contents to be;

$$\text{VPI-5} \quad 25\%$$

$$\text{AlPO}_4\text{-8} \quad 17\%$$

These data meant that the quantitative estimation of $\text{AlPO}_4\text{-8}$ content could be made very accurately, more accurately than estimations of impurity content in Chapter 3, where water contents of the different phases had not been measured so accurately. Table 4.1 lists the data used in the construction of the calibration curve.

Table 4.1 Data used for the construction of the calibration curve

% $\text{AlPO}_4\text{-8}$	Peak Heights				ln of Peak ratio ^a
	$2\theta = 10.8$	$2\theta = 18.8$	$2\theta = 6.2$	$2\theta = 9.9$	
11	8.5	5.1	0.8	0.8	2.14
21.5	7.8	4.8	1.5	1.5	1.43
32	6.2	3.6	1.9	1.9	1.18
42.3	5.6	3.4	2.3	2.4	0.67
52.4	4.4	2.5	2.9	3.1	0.14
62.2	4.2	2.4	3.8	4.0	-0.17
72	3.0	1.7	4.7	4.6	-0.68
81.5	2.6	1.4	4.8	5.0	-0.90
90.8	1.4	0.9	5.8	5.8	-1.62

^a The peak ratio was the sum of the VPI-5 peak heights (10.8 and 18.8) vs the sum of the $\text{AlPO}_4\text{-8}$ peak heights (6.2 and 9.9).

Figure 4.7 shows the plot obtained from the above data which, as in Chapter 3, was found to give a straight line. $\text{AlPO}_4\text{-8}$ levels in heated samples of VPI-5, derived from the calibration plot, are detailed in Table 4.2..

Figure 4.7 Calibration plot of AlPO₄-8 in VPI-5.

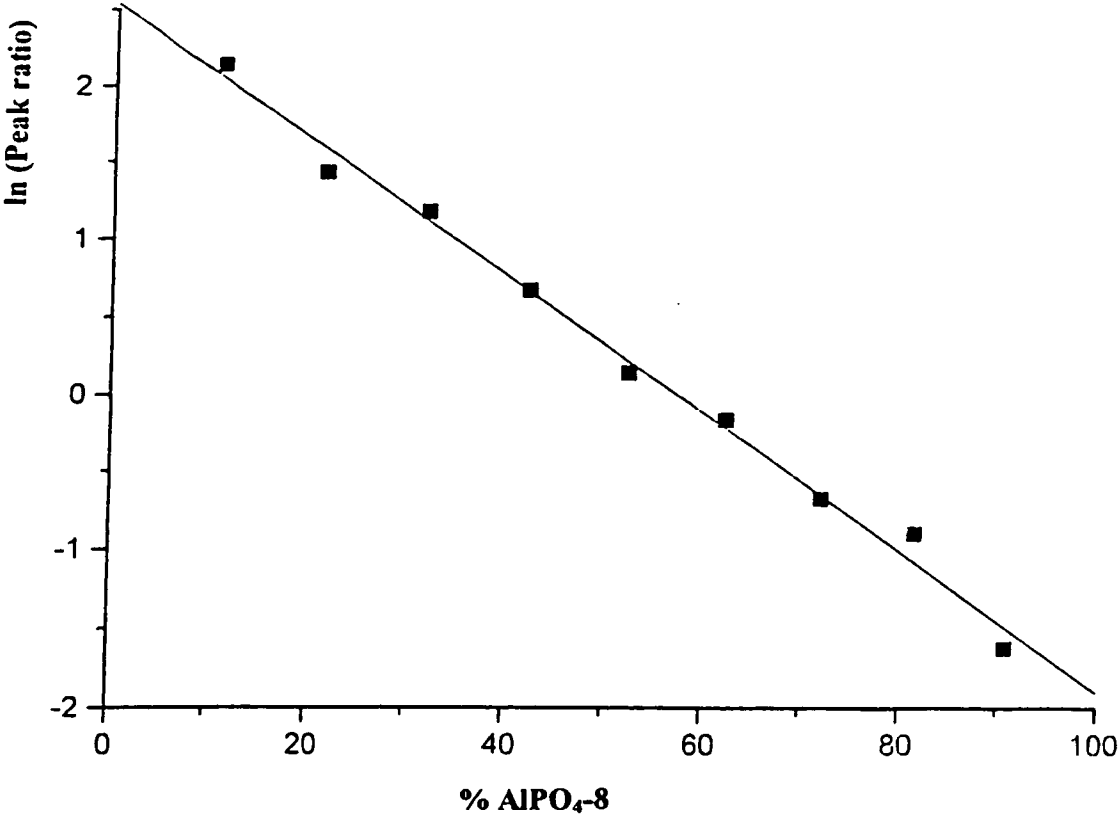


Table 4.2 AlPO₄-8 levels in heated samples of VPI-5, as determined by reference to the calibration plot.

Temp / K	Time / hr	VPI-5 / %	Time / hr	VPI-5 / %	Time / hr	VPI-5 / %	Time / hr	VPI-5 / %
338 (65°C)	24	86	48	35	72	14	-	-
353 (80°C)	8	92	9	70	12	63	-	-
368 (95°C)	3	88	4	55	5	51	6	37
383 (110°C)	1	88	1.5	59	2	45	3	10

Once the levels of VPI-5 had been determined, it was realised that the transformation appeared to be first order and that it would therefore be possible to determine the activation energy of the transformation. The rate constants were calculated by plotting $\ln [\text{VPI-5}]$ vs time, with initial $[\text{VPI-5}]$ taken as equal to 1, where $\ln[A]/[A]_0 = -kt$ according to the first order rate law. These plots are shown in Figure 4.8. Finally Figure 4.9 shows how, following the Arrhenius equation, a plot of $\ln k$ vs $1/T$ was used to determine the activation energy.

$$\ln k = \ln A - E_a/RT \quad (\text{The Arrhenius equation})$$

Thus, the activation energy for the transformation of DPA-synthesised VPI-5 to $\text{AlPO}_4\text{-8}$ was determined to be:

$$80 (+/- 6) \text{ kJ mol}^{-1}$$

This figure is very different to that reported by He *et al* [20] for DPA-VPI-5, who calculated the activation energy for the transformation to be 273 kJ/mol. They used a sample tube of dimensions 40 - 50 mm length by 12 mm diameter and made of PTFE / aluminium or of glass, set in a copper block which was heated by circulating silicone oil. The temperature of the sample was recorded by a thermocouple probe which just touched its upper surface. XRPD data to follow the transformation of VPI-5 to $\text{AlPO}_4\text{-8}$ were collected in situ at temperatures of 135 and 155°C.

A possible reason for the different values is that He *et al* had much more scope for errors to creep into their work. Their samples seem to have been quite large, to judge by the dimensions of the sample tube, this could have greatly slowed the rate of water loss. Also, despite the large size of the samples they recorded the temperature of the VPI-5 by means of a thermocouple probe just touching the surface. The two temperatures which they used were high (135 and 155°C) which led to very short half-lives for the transformation (as low as 15 minutes) and the problem of few data points. The short half-lives and the position of the thermocouple meant that there was much scope for overestimation of the temperature within the bulk of the sample. Such errors would cause the calculated activation energy to be larger than the actual.

By the use of very small samples, spread thinly, and heated at four, lower temperatures, such errors were minimised in this work. Despite this, however, the activation energy which has been calculated here may only be an apparent energy, for the temperatures at which the samples were heated, and may only be relevant to the particular batch of VPI-5 used for the experiments. The reason for this is because so many factors appear to influence the transformation process that some are liable to vary every time VPI-5 is heated.

Figure 4.8 Plots of the rate of transformation of VPI-5 to $\text{AlPO}_4\cdot 8$ at different temperatures.

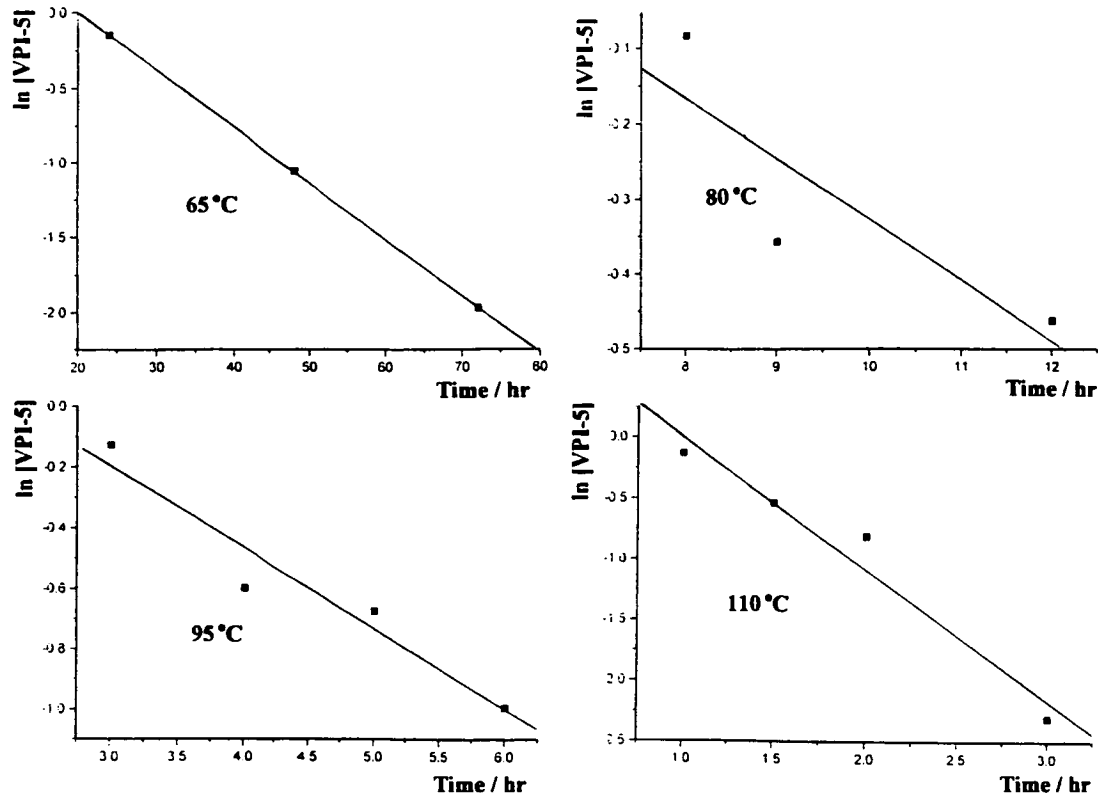
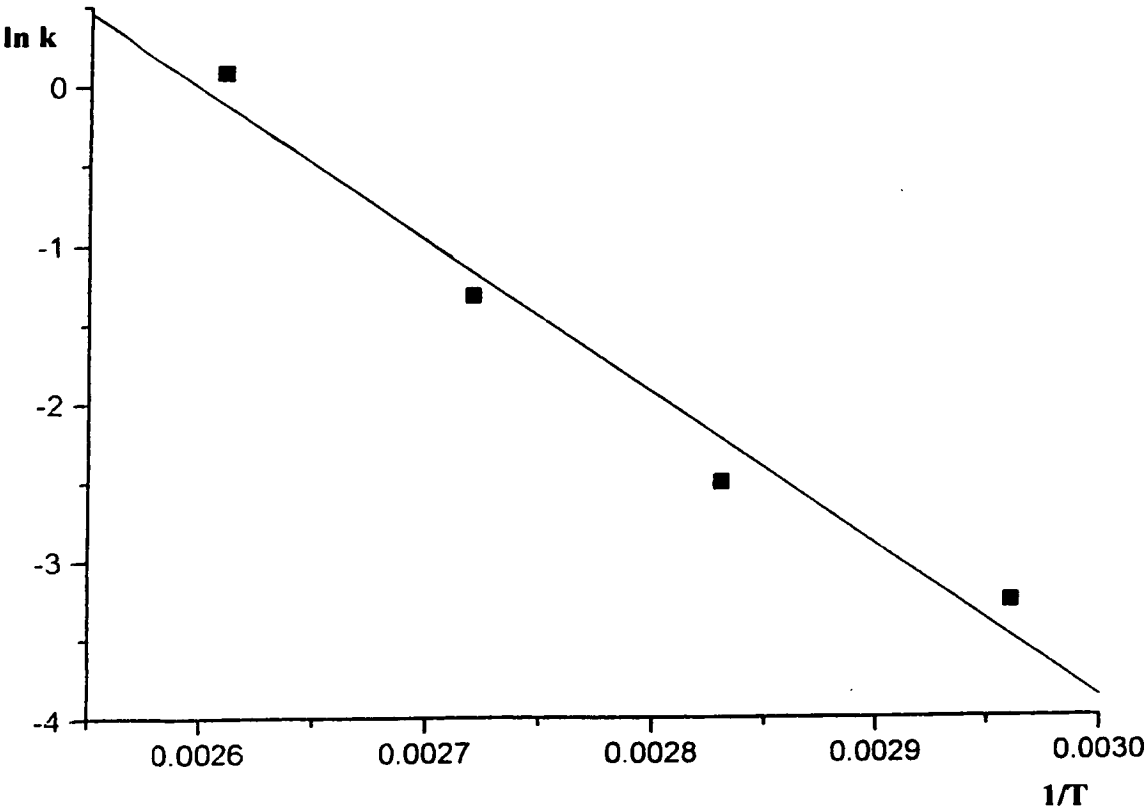


Figure 4.9 A plot of $\ln k$ vs $1/T$ for heated VPI-5.



The Thermal Stability of DPA-VPI-5

All nominally identical batches of DPA-synthesised VPI-5 were tested for their thermal stability at the relatively low temperatures used for activation energy determination in the previous section and were found to show similar stability. The thermal stability of VPI-5 was also tested under a variety of other conditions: It was heated to temperatures between 400°C and 1200°C at rates which varied from 10°C per minute to flash heating of small samples in preheated ovens. Most of the heating to determine thermal stability involved the methods outlined in Chapter 2. No method was found which could dehydrate VPI-5 without loss of structure, which in almost all cases was total loss. $\text{AlPO}_4\text{-8}$ was the product up to about 1000°C, above that the $\text{AlPO}_4\text{-8}$ was itself converted to $\text{AlPO}_4\text{-tridymite}$. Figure 4.10 shows scanning electron micrographs which illustrate how there was no visible change of crystal shape when VPI-5 transformed to $\text{AlPO}_4\text{-8}$.

In order to present a larger surface area to sorbates it was deemed necessary that the large wheatsheaves of DPA-VPI-5 needed to be ground in a mortar and pestle. The thermal stability of ground VPI-5 was checked in case grinding led, through faster water loss, to more rapid transformation to $\text{AlPO}_4\text{-8}$. It was found that grinding had no noticeable effect.

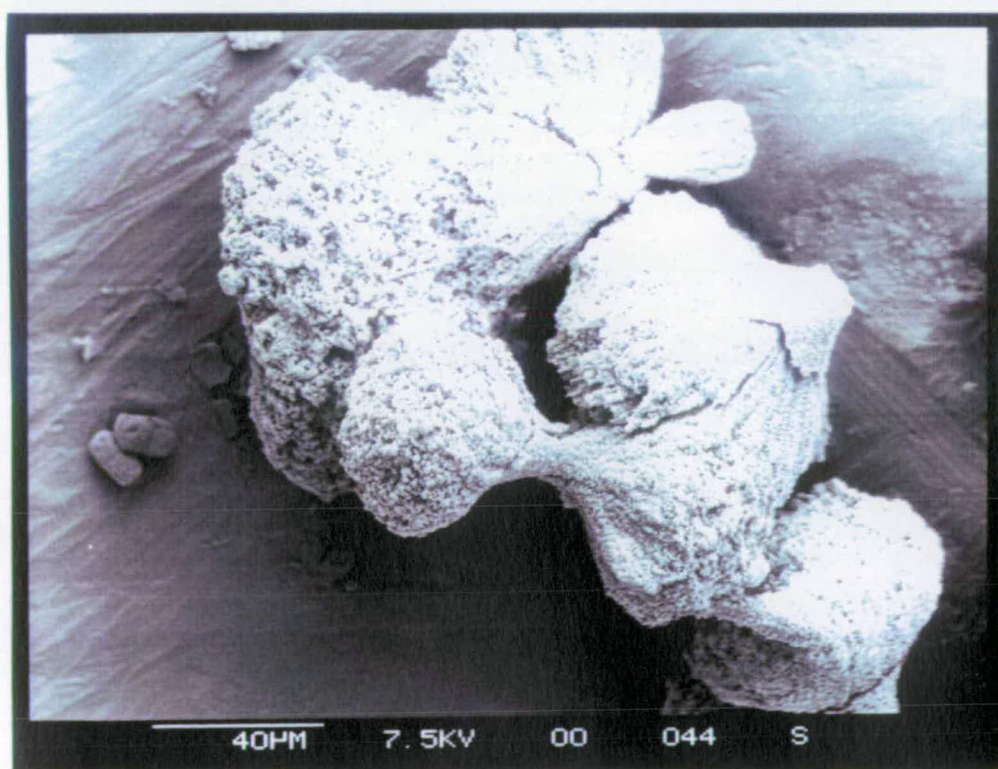
Independently of the work described in the introduction, it was discovered in the course of this project that the transformation of VPI-5 to $\text{AlPO}_4\text{-8}$ was not solely dependent upon temperature, but that the key factor was loss of water from the structure. This was shown to be so by heating VPI-5 at a range of temperatures as high as 141°C in sealed glass tubes. As has already been seen, at temperatures as low as 65°C, transformation to $\text{AlPO}_4\text{-8}$ occurred when VPI-5 was heated in open tubes. In this study no sample which was contained in a sealed tube showed any sign of $\text{AlPO}_4\text{-8}$ formation even when heated for 8 days at 141°C.

It was correctly suggested that the reason for this was that only the loss of structural water from VPI-5 leads to transformation, not water loosely held in the pores, and that the loss of structural water is prevented in a sealed tube due to a high partial pressure of water formed when the physisorbed pore water desorbs. It was just after the completion of that work that the paper was published by Akporiaye *et al* [18] which detailed a similar study and came to the same conclusions. They tightly packed VPI-5 into a sealed ampoule and heated it to 110°C without any transformation to $\text{AlPO}_4\text{-8}$. In fact it was not necessary to tightly pack the VPI-5, for the samples heated in this work to 141°C only occupied a small amount of the volume of their sealed tubes.

Figure 4.10 Scanning electron micrographs of VPI-5 and AlPO_4 -8.



AlPO_4 -8



VPI-5

The Stability of Evacuated VPI-5

As was stated in the introduction to this chapter, it was claimed by Annen *et al* [10] that VPI-5 would be successfully dehydrated without loss of structure if it was evacuated at around 10^{-5} Torr. Since the use of a vacuum line had potential as a way of mobilising dyes at low temperatures, and so aiding their sorption into VPI-5, the claim was tested. Small samples of several different batches were evacuated at room temperature for up to 48 hours. After removal from vacuum and rehydration they were examined by XRPD.

The pressure in the line was found to be a crucial factor in the stability, presumably because it affected the rate at which water was removed. If the line was not performing well then the pressure only got down to around 10^{-3} to 10^{-4} Torr; in these cases there was some $\text{AlPO}_4\text{-8}$ formation in the samples. Once pressures of 10^{-5} Torr or less were achieved then evacuation at room temperature was successful. A few attempts were made to thoroughly dehydrate the evacuated VPI-5 by gentle heating, however the heater control apparatus used was not sufficiently sensitive for the work. This resulted in much higher temperatures than was desired, with the consequence that all of the heated samples partially transformed to $\text{AlPO}_4\text{-8}$.

As an adjunct to this section it was found that VPI-5 was also unstable in the gently dehydrating conditions of an evacuated desiccator. Samples placed in such a desiccator for six weeks at room temperature, over P_2O_5 , were found to have largely transformed to $\text{AlPO}_4\text{-8}$.

The Effect of Ultrasound upon VPI-5

Ultrasonification is a technique which has been used to increase the rate of intercalation of organic compounds into layered inorganic hosts [22]. This made ultrasound a potential method of assistance in getting organics into VPI-5. However it has also been shown [23] that ultrasound can create substantial surface damage in susceptible materials. A sample of VPI-5 was slurried in water and ultrasonically irradiated for 30 minutes with a 20kHz direct immersion horn. The recovered crystals were analysed by microscopy and by XRPD in order to assess whether any damage had occurred.

Microscopy showed that some VPI-5 particles had broken up, but that overall there was little damage. XRPD showed the VPI-5 framework to be intact.

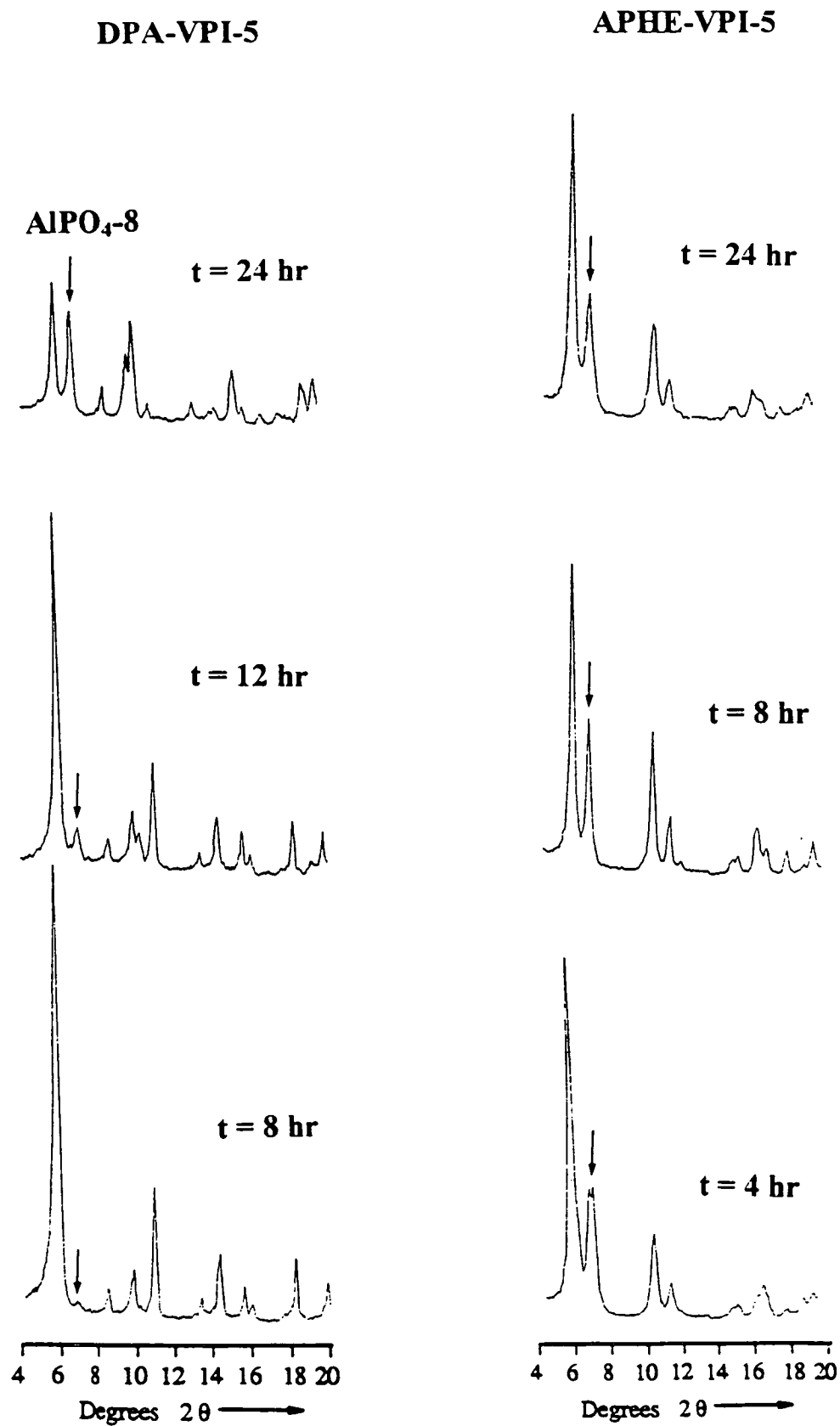
4.2.2 The Thermal Stability of APHE-synthesised VPI-5

The thermal stability of APHE-VPI-5 was investigated under a similar range of conditions to those used for DPA-VPI-5. It was found that for all temperature regimes no sample of APHE-VPI-5 was 100% converted to $\text{AlPO}_4\text{-8}$, even after prolonged heating or repeated cycles of heating, cooling and rehydration. This was determined by the fact that the XRPD peaks at $2\theta = 10.8$ and 18.8 did not disappear.

The inability to convert a sample of APHE-VPI-5 completely to $\text{AlPO}_4\text{-8}$ meant that it was not possible to mix APHE-VPI-5 and APHE-VPI-5-derived $\text{AlPO}_4\text{-8}$ in order to construct a standard graph with which to accurately determine the $\text{AlPO}_4\text{-8}$ content of heated samples. Because of the differences in relative peak intensities between DPA-VPI-5 and APHE-VPI-5 it was not possible to use the previous standard graph to estimate the degree of transformation. Neither was it possible to mix DPA-VPI-5-derived $\text{AlPO}_4\text{-8}$ with APHE-VPI-5 because of the very different bulk morphologies of the two materials, i.e. one (DPA) was quite a dense material, whereas the other (APHE) was very bulky and also difficult to grind because it clumped together so strongly. In fact similar weights of the two materials occupied very different volumes, that of APHE-VPI-5 was several times greater than that of DPA-VPI-5. Thus no accurate quantitative measurements could be derived for APHE-VPI-5.

Despite this, measurement of peak ratios showed that heated APHE-VPI-5 reached a plateau level of $\text{AlPO}_4\text{-8}$ content which was estimated to be high, approximately 85%. Thus, in terms of the amount of $\text{AlPO}_4\text{-8}$ formed, APHE-VPI-5 appeared to be more stable than DPA-VPI-5. However, as Figure 4-11 shows, there seemed to be an anomaly in that the $\text{AlPO}_4\text{-8}$ in APHE-VPI-5 was formed very quickly, far faster indeed than in DPA-VPI-5.

Figure 4.11 A comparison of $\text{AlPO}_4\text{-8}$ formation in DPA-VPI-5 and APHE-VPI-5 heated at 80°C .



4.3 Stability after Post-synthesis Treatment

It seemed that the controllable factors which affected the stability of VPI-5 were one or both of ;

- i) a disordered water structure in the pores [14]
- ii) the presence of impurities in the crystals [13].

A number of techniques were employed to try and improve the thermal stability, some were novel and although others were similar to methods already described in 4.1, the results achieved in this project are worth description.

4.3.1 DPA-VPI-5

Experimental

The main hope of improved stability seemed to lie with some sort of washing technique. The two options studied were the use of water or the use of an organic solvent. Reasons for these choices were as follows:

- i) If the main problem lay with a disordered pore water structure then water washing was most likely to succeed.
- ii) If occlusion of n-dipropylamine during synthesis was the main controllable factor then an organic solvent was most likely to remove the DPA, since it is immiscible with water.

The stability of VPI-5 in the presence of organic solvents would also be a useful area of study since any future work to sorb dyes into VPI-5 might require their use.

Three types of wash were used, they were:

- i) cold wash of a slurry of VPI-5;
 - ii) hot wash of a slurry of VPI-5;
 - iii) soxhlet extraction of VPI-5.
- i) VPI-5 (0.2g) was slurried with each of water, acetone, ethanol, methylene chloride or diethyl ether (100ml) and the slurries were stirred for 48 hours. The crystals were recovered by filtration and air-dried.

ii) VPI-5 (0.3g) was slurried with each of water, ethanol or acetone (150ml) and the slurries were boiled for 4 hours. A further slurry of VPI-5 (1g) in water (150ml) was boiled for 9 hours. Again the crystals were recovered by filtration and air-dried.

iii) VPI-5 (0.3g) was placed in a cellulose thimble and solvent extracted for 7 hours with water, ethanol or methylene chloride. The samples were air-dried in the thimbles. A further sample of VPI-5 (1g) was soxhlet extracted with water for 9 hours.

Once dried, all of the samples were analysed by XRPD to determine whether the treatments had affected their crystallinity. In order to investigate the thermal stability, small amounts of each of the washed samples were heated at 80°C for varying lengths of time and, after cooling and rehydration in ambient conditions, were analysed by XRPD. Some of the samples which had been treated with water underwent further investigation, they were subjected to thermogravimetric analysis (TGA) and also had their thermal stability tested at higher temperatures than 80°C. Note that TGA involved heating the samples to 950°C and so the recovered material was analysed to give further thermal stability data.

In a final study of the post-synthesis conditions which affected the stability of VPI-5, the following experiment was carried out:

A portion of as-synthesised VPI-5 was taken from batch VS13. Part of the portion was retained in its as-synthesised state (designated VRE-1), the remainder was slurried with water and boiled for 5 hours (VRE-2). Part of VRE-2 was retained and the rest was soxhlet-extracted with ethanol for 5 hours (VRE-3). Again the sample was split, part being retained and the remainder being slurried in water and boiled once more for 5 hours (VRE-4). The thermal stability of the four samples was examined and they underwent thermogravimetric analysis.

This experiment gave an opportunity to assess which factor was most important in improving the stability of VPI-5, the creation of a well-ordered pore water structure or the removal of synthesis impurities.

Results

Examination of washed crystals by XRPD showed the VPI-5 structure to have remained intact in all cases. Once they had been heated to 80°C differences became apparent.

- i) All of the cold-washed samples remained as unstable as the starting material.
- ii) Samples washed with hot organic solvents showed no stability gain, but those washed with hot water appeared to be more stable when heated at 80°C than as-synthesised VPI-5.
- iii) The same results were obtained from soxhlet extracted samples as from the hot-washed samples.

Although conditions in the soxhlet were more gentle than in the heated slurry, it was thought that if removal of impurities was the main route to improved stability then extraction might be the more effective route. In fact after a close examination of the XRPD patterns of heated samples it was concluded that the slurry route was marginally more effective. Table 4.3 details the amounts of $\text{AlPO}_4\text{-8}$ formed in some different samples upon heating.

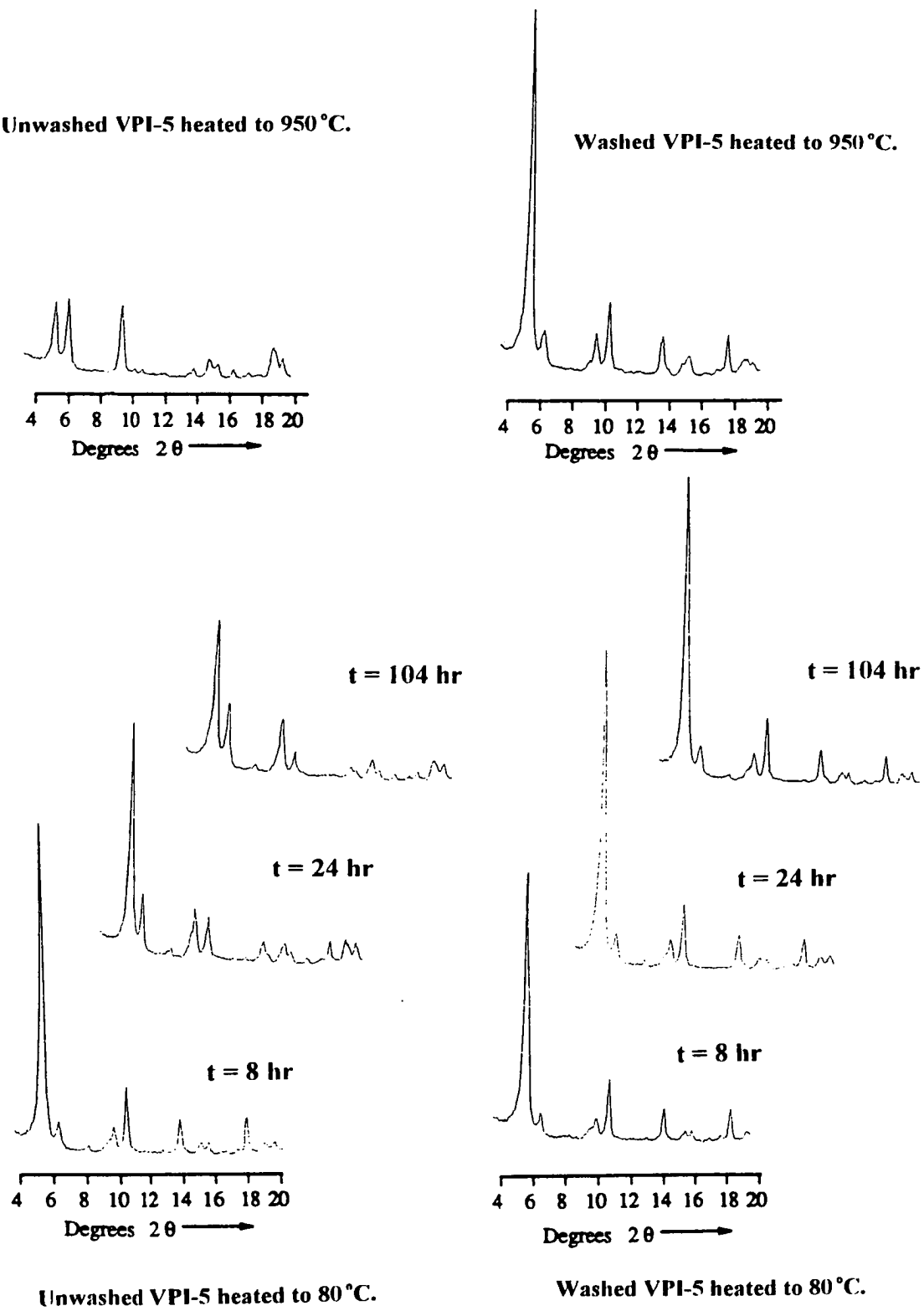
Table 4.3 % $\text{AlPO}_4\text{-8}$ in heated VPI-5 samples

Heating conditions → Sample ↓	80°C/5hr	80°C/8hr	80°C/24hr	80°C/104hr	950°C
As made	-	40	67/86	100	100/100
Heated slurry with water	27	39	41/45/100	45	47/96
Soxhlet -extracted with hot water	52	45	52/100	55	79

Note that all samples were made from the same batch of VPI-5 (VS6).

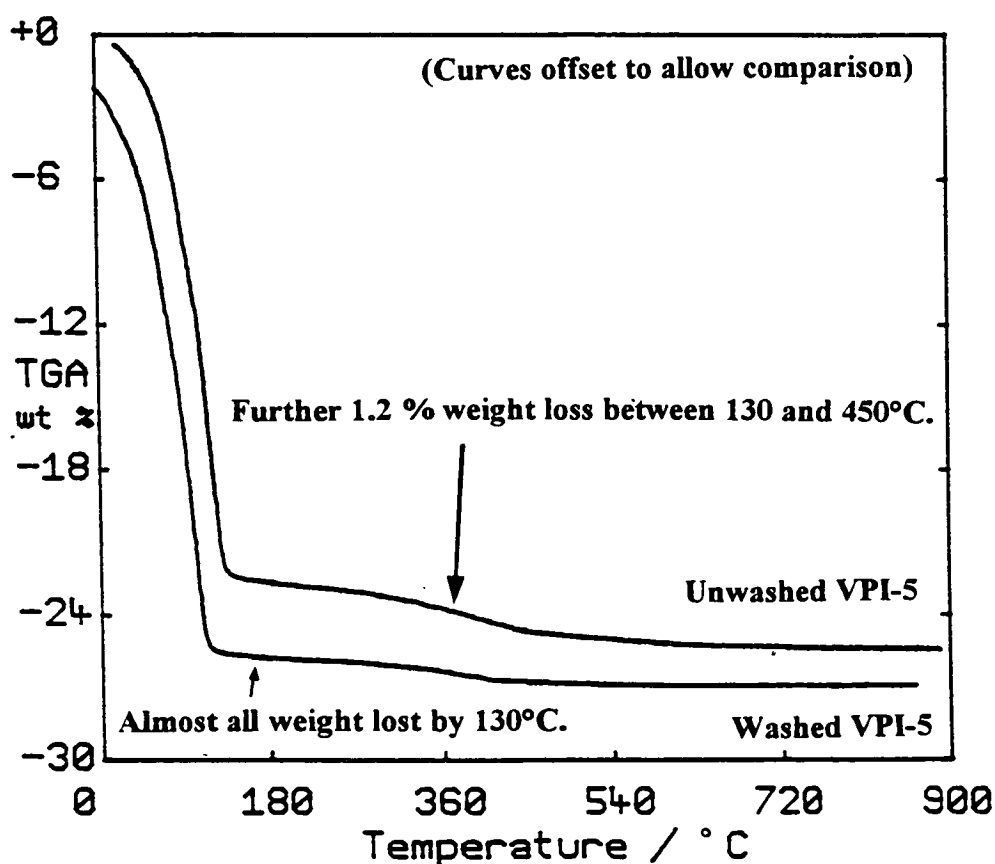
The general trend towards increased stability can clearly be seen despite the fact that there were several inconsistent results. The washed samples usually seemed to reach a plateau level of $\text{AlPO}_4\text{-8}$ content when heated at the gentle conditions of 80°C, and that even when subjected to harsher conditions they did not quite transform entirely to $\text{AlPO}_4\text{-8}$. This point is illustrated further in Figure 4.12.

Figure 4.12 The effect of washing upon the thermal stability of DPA- VPI-5.



Thermogravimetric analysis of as-made and water-washed samples showed that there was a difference in weight loss behaviour between the two classes of sample. The difference was small, but it was seen consistently and was therefore considered to be significant. What was seen was that, although the total weight loss of washed samples was nearly the same as the total weight loss for the unwashed parent, for washed samples almost all loss occurred by 150°C whilst the parent samples showed slightly less weight loss by 150°C but had a small step around 350°C. This feature was only small (~0.5% - 2%) but, as was stated above, it was seen consistently, an illustrative example is shown in Figure 4.13. The step suggests the presence of occluded material other than water and so supports the finding of Davis and Young [13] when they stated that the removal of impurities led to less $\text{AlPO}_4\cdot 8$ formation.

Figure 4.13 TGA curves of washed and unwashed DPA-VPI-5.



Effects of different washing regimes. The samples VRE1 - VRE4, which underwent different washes, were heated under a variety of conditions. Table 4.4 details the amounts of $\text{AlPO}_4\text{-8}$ which formed in the samples. These results are further illustrated in Figures 4.14 and 4.15

Table 4.4 The thermal stability effects of consecutive washes with water and ethanol.

Heating conditions →	% $\text{AlPO}_4\text{-8}$			
	80°C/24hr	80°/104hr	750°C	950°C ⁻¹
VRE1	89	100	100	100
VRE2	0	22	70	60
VRE3	100	100	100	70
VRE4	0	20	72	30

The results show very strong evidence that it is necessary to wash VPI-5 in water to improve its thermal stability. Figure 4.16 shows the thermal analysis curves for the samples prepared in this experiment. The TGA curves show that all of the samples lost about the same amount of weight (25%) when heated to 900°C. For VRE-1 about 2% of its weight was lost in the step at around 350°C, whilst the other three samples showed almost all weight loss occurred by 180°C. Thus the large difference in thermal stability between VRE-1 and VRE-2 can be accounted for by the removal of material, most probably the synthesis structure director, di-n-propylamine, which was occluded in the pores during synthesis.

Further evidence suggests, however, that it was not the specific nature of the occluded material which caused the lack of stability. This conclusion is reached because of the low thermal stability of VRE-3. This sample, a portion of VRE-2 which had been soxhlet extracted with ethanol, had thermoanalytical curves which were very similar in shape to those of VRE-2, yet its thermal stability was vastly inferior. Close inspection showed that there were, in fact, very small differences between the curves. When a portion of VRE3 was then washed with hot water, to give VRE4, the thermoanalytical curves became identical to those of VRE2 and high thermal stability was regained.

Figure 4.14 The effect of different washing regimes upon the thermal stability of DPA-VPI-5 heated at 80 °C for 104 hr.

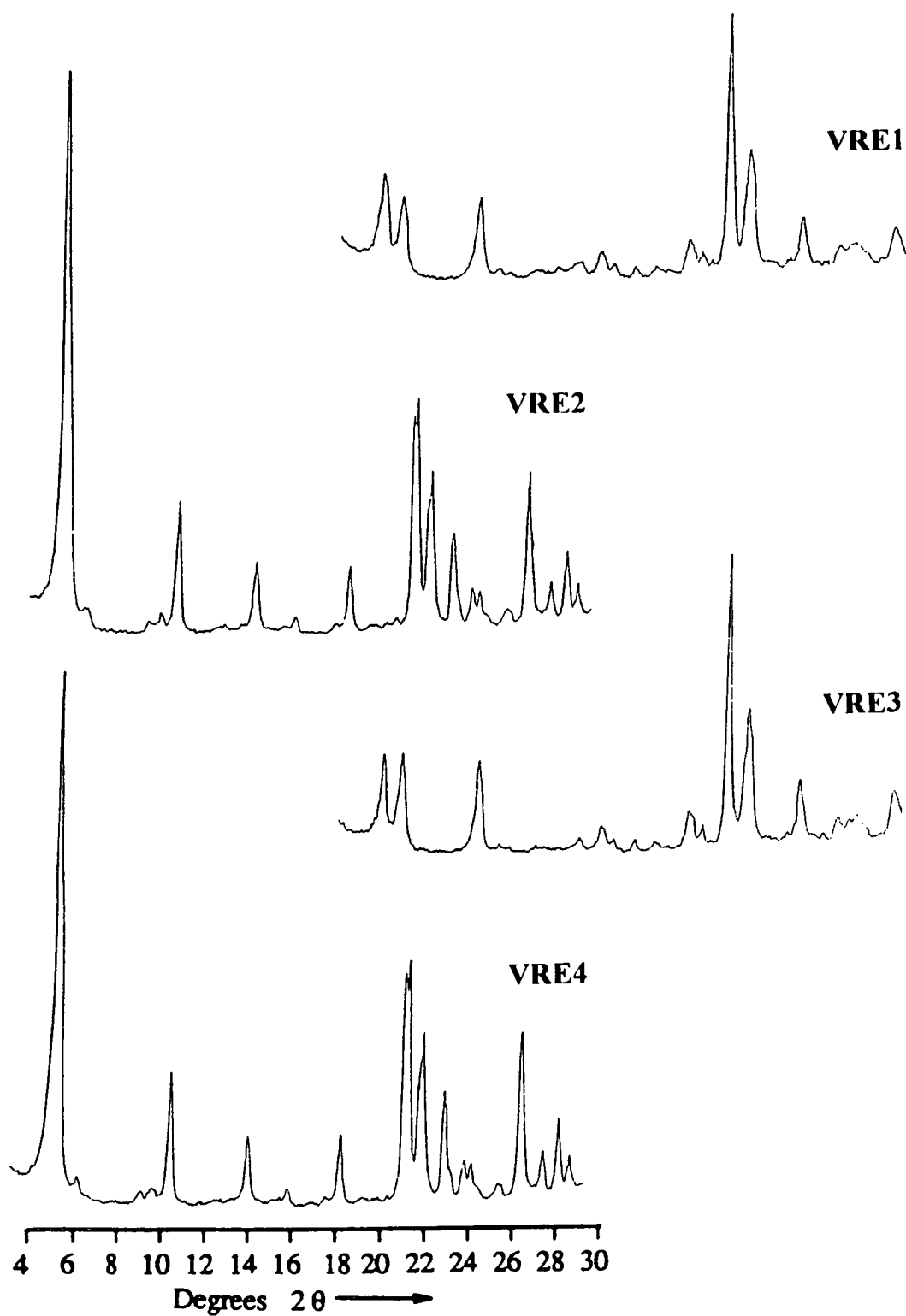


Figure 4.15 The effect of different washing regimes upon the thermal stability of DPA-VPI-5 heated to 750 °C.

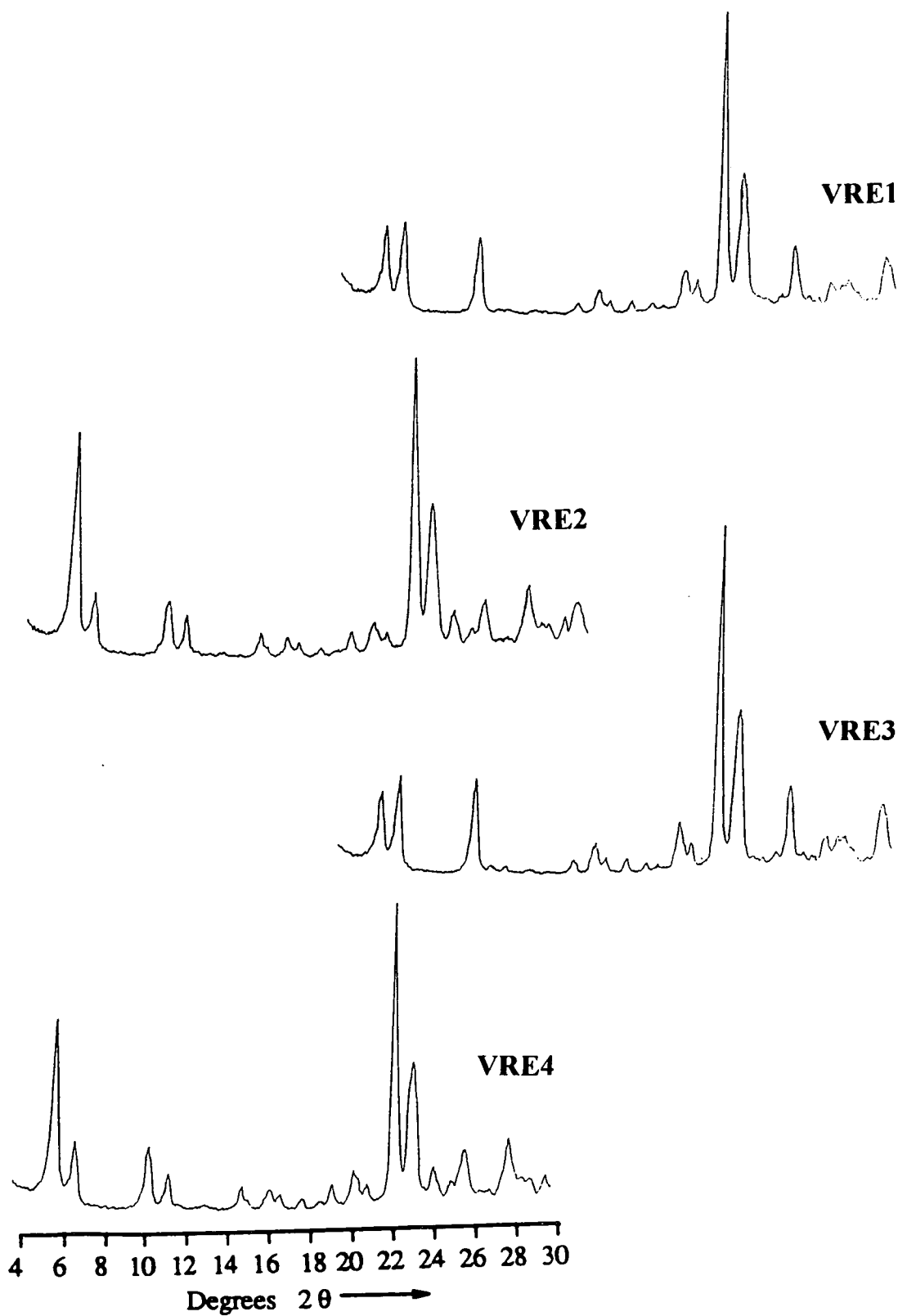
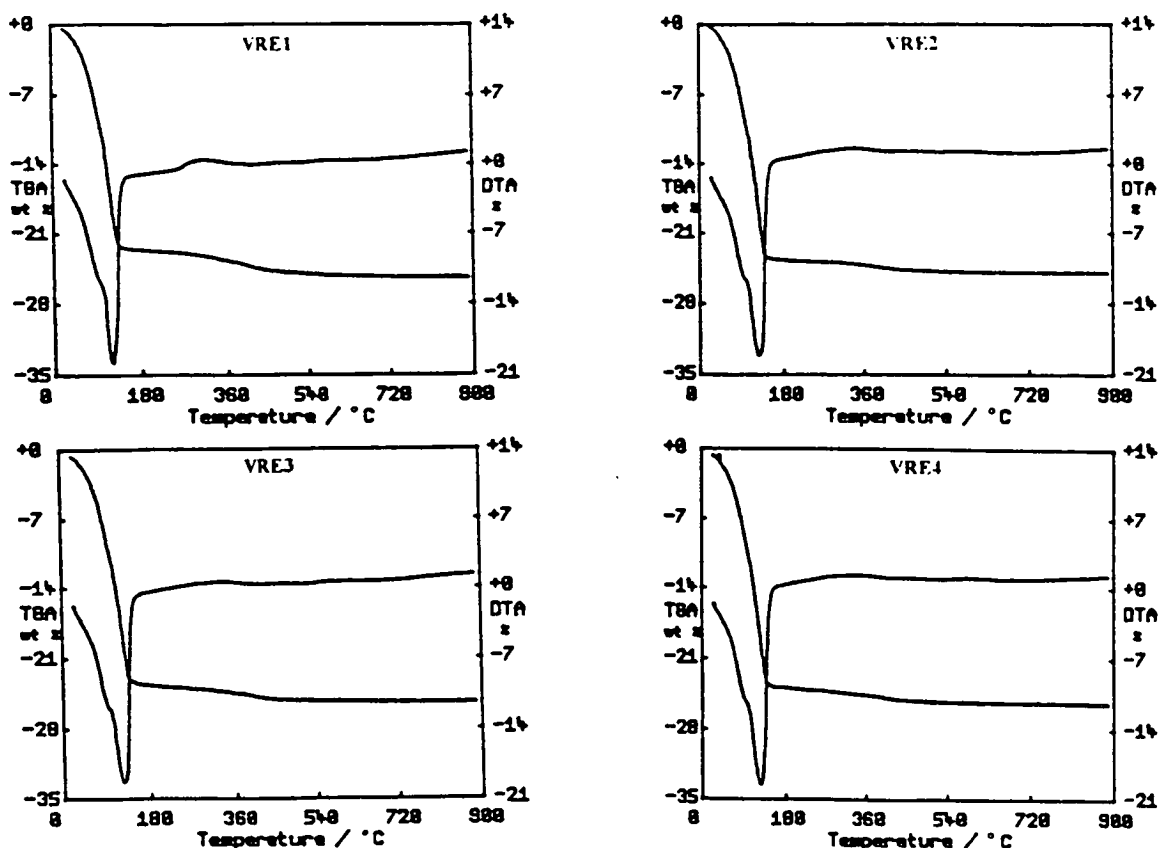


Figure 4.16 TGA and DTA curves of the washed samples VRE1 - 4.



These results are consistent with uptake of some ethanol into the pores of VPI-5. Thus it was shown that it was not just the presence of synthesis impurities which lowered the thermal stability of VPI-5. The presence of small amounts of the simple solvent ethanol had the same effect without sharing any of the chemistry of di-n-propylamine. It is therefore concluded that synthesis impurities in VPI-5 do not positively aid the transformation process to $\text{AlPO}_4\text{-8}$, but that their presence disrupts the pore-water structure and so the hypothesis of Potvin *et al* [15] was correct when they said that washing out of impurities led to a more ordered triple helix of water which in turn aided thermal stability.

A general result seen in work which investigated the thermal stability of VPI-5 was that even the best increases in stability were not that great: $\text{AlPO}_4\text{-8}$ was still formed, albeit in smaller quantities, and transformation still took place at relatively low temperatures. However, any increase in stability was a bonus and so all VPI-5 was boiled in water prior to use. The effects of boiling on different batches of VPI-5 were seen to be variable, as is shown in Table 4.5.

Table 4.5 Effects of boiling on VPI-5

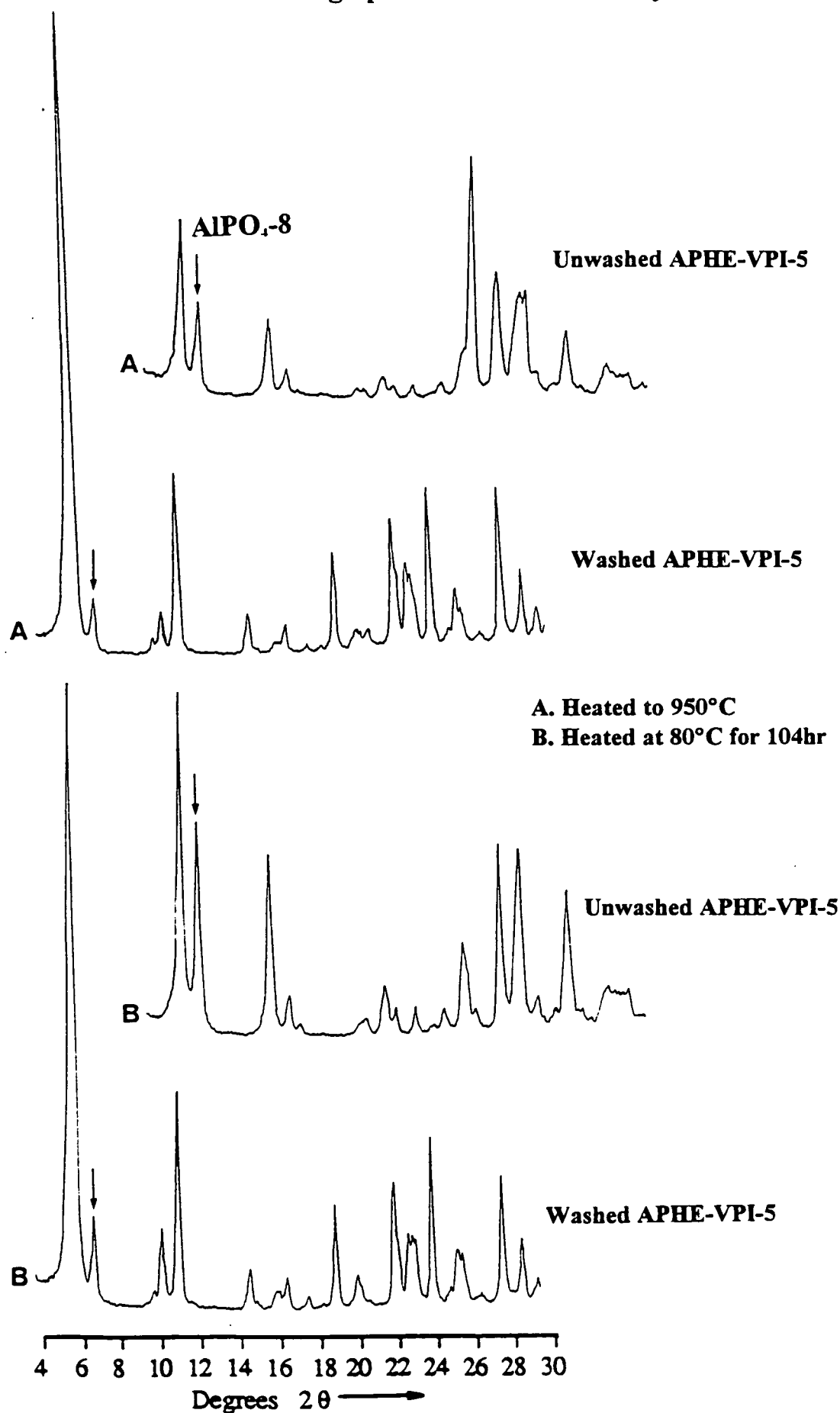
Batch	% $\text{AlPO}_4\text{-8}$ after 24hrs at 80°C
VS5	45
VS6	43
VS13	25
VS14	55
VS15	65

4.3.2 APHE-VPI-5

Most of the work on the effects of post-synthesis treatments upon the stability of DPA-VPI-5 had already been done by the time that work commenced with APHE-VPI-5. For that reason, only the effects of water washes were explored, the methods which were used being heated slurries and soxhlet extraction, *i.e.* those which had proved most successful with DPA-VPI-5. As was stated in section 4.2, APHE-VPI-5 in its as-synthesised state, appeared to be more stable than DPA-VPI-5, since no sample was found to convert totally to $\text{AlPO}_4\text{-8}$ when heated.

It was found that washing the crystals with hot water led to improved stability. As before, both techniques (soxhlet extraction and boiling water) seemed to be close in their effectiveness and also to show variations between batches in the degree of stability which was conferred. Upon close examination boiling a slurry was seen to be the more consistent of the two methods and so again it was chosen for use on all batches of APHE-VPI-5 prior to further use of them. Figure 4-17 compares the XRPD traces of washed and unwashed APHE-VPI-5 subjected to a range of heating conditions. It shows the washed material to be much more stable, with the estimated plateau level of $\text{AlPO}_4\text{-8}$ averaging about 40% compared with greater than 80% for the unwashed samples. Thus, as with DPA-VPI-5, it was found that when the product was boiled in water for a period of hours there was a subsequent increase in its thermal stability.

Figure 4.17 The effect of washing upon the thermal stability of APHE-VPI-5



4.4 Conclusions

A thorough investigation was made into the thermal stability of VPI-5 and into ways by which it could be improved. In the course of this work an activation energy was determined for the transformation of DPA-VPI-5 to $\text{AlPO}_4\text{-8}$. The figure was:

$$80 \text{ kJmol}^{-1}$$

This was very different to the only previously reported figure for DPA-VPI-5 [14] and, although thought to be based on more reliable data, ^{88 kJmol^{-1}} may only be an apparent activation energy. It would be of great interest if further work were to be carried out which could clarify the situation.

DPA-VPI-5, in its as-synthesised form, was found to be a very unstable material which was easily transformed totally to $\text{AlPO}_4\text{-8}$, even at room temperature. APHE-VPI-5 was seen to be a more stable material, XRPD showed that it never transformed completely to $\text{AlPO}_4\text{-8}$. It did however seem that the initial transformation of APHE-VPI-5 to $\text{AlPO}_4\text{-8}$ was faster than for DPA-VPI-5. In a study of two different types of amine-synthesised VPI-5, He *et al* [20] gave a good reason as to why the apparently more stable material should transform more quickly. They stated that P-OH groups in the poor framework distort the framework such that bond rearrangement is hindered and so the more unstable structure takes longer to transform to $\text{AlPO}_4\text{-8}$.

Many of the findings of other workers, reported during the course of this project, were supported by these results. The most significant of these are thought to be:

- i) The stability of VPI-5 can be increased by boiling VPI-5 in water for several hours, although the effect is variable from batch to batch.
- ii) The process of transformation requires the loss of water, as opposed to being a hydrolysis process. This was shown by the experiment in which a sealed sample of DPA-VPI-5 was heated to 141°C for 8 days without any sign of $\text{AlPO}_4\text{-8}$ formation. This fits in with the theory of Brunner [21] as to why a transformation should take place. It should be stated however that this cannot be the entire story since it would imply that dehydrated VPI-5 could *easily* transform to $\text{AlPO}_4\text{-8}$, which has been shown [10] not to be the case.

The reasons for the importance of the above two findings to this project were: The implementation of (i) led to improved starting material for further experiments. The discovery of (ii) meant that experiments could be designed such that the rate of water loss was stopped or slowed significantly when VPI-5 needed to be heated and so $\text{AlPO}_4\text{-8}$ formation could be prevented or at least minimised. This proved to be of more importance to the rest of the project than the initial aim of finding good temperatures for putting dye into VPI-5, ones which gave a good trade-off between slow rate of transformation to $\text{AlPO}_4\text{-8}$ and high dye mobility.

As an aside it should be noted that the construction of a calibration curve for the determination of the $\text{AlPO}_4\text{-8}$ content of samples of DPA-VPI-5 showed that at significant levels of $\text{AlPO}_4\text{-8}$, up to 20-30%, the $\text{AlPO}_4\text{-8}$ peaks in XRPD patterns were very small. Thus some workers may have misjudged the amount of $\text{AlPO}_4\text{-8}$ formation in their heated samples, for example Annen *et al* [10], to judge from the XRPD patterns which they published, were probably wrong to claim that only minimal $\text{AlPO}_4\text{-8}$ formation was observed in the sample of VPI-5 which they heated rapidly in ambient air.

Although the benefits of hot-washing VPI-5 were first published in 1991 [10] there is still debate on the subject and in fact in a recent paper [24] it was reported that the authors were unable to obtain thermally stable samples of VPI-5 after boiling in water. What seemed to have happened was that the thermal conditions which were used were too harsh to show up the sort of stability improvements which occur. What was concluded from the work presented here was the following:

The thermal stability of VPI-5 was increased by boiling in water, but the increases were only incremental, *i.e.* the formation of $\text{AlPO}_4\text{-8}$ was not totally prevented and the temperatures at which transformation occurred did not increase. What did happen was that plateau levels of $\text{AlPO}_4\text{-8}$ formation were reached such that under relatively gentle conditions, *i.e.* low temperatures or high temperatures with fast heating rates so that water was removed quickly, much of the VPI-5 remained intact.

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Chapter 5

The Sorption of Dyes into VPI-5

5.1 Introduction

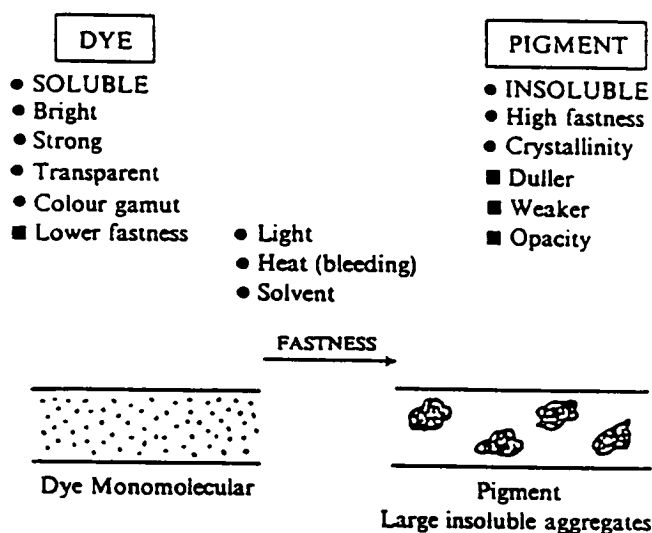
As was said in Chapter 1, the act of constraining organic molecules within molecular sieves has been seen to be able to cause various effects upon them, with regard to their spectra, photosensitivity and /or photoreactivity, and their thermal stability. The aim of this work was to find effective methods by which dyes could be sorbed into VPI-5 and then to look for such novel effects from the sorbed dyes. Such effects would have potential benefits for a range of applications. These applications can be split into those for dyes trapped within the framework, that is clathrated, and those for dyes sorbed into the channels, but which can readily desorb.

Encapsulated dyes could find uses, for example, as novel pigments. These are important because of the limited number of dyes available for use in plastics due to the problems of their decomposition at processing temperatures, photodegradation, and migration of dye.

It should be noted here what the difference is between a dye and a pigment. The classical definition is that a dye can be dissolved and is usually applied from solution whereas a pigment remains completely insoluble. Gregory [1] describes the advantages and disadvantages of these different colourants and his views are summarized in Figure 5.1. The advantages of dyes are that they are bright, tinctorially strong, transparent and cover a very large colour-gamut. Their main deficiencies are lower fastness to agents such as light, heat, and solvents. As shown in Figure 5.1 the explanation for most of these properties is that, being soluble, dyes are generally present in the monomolecular state and thus present a large surface area which gives strong colour but also makes it easy for light and solvents to attack.

Pigments tend to be fast to these agents since they are large insoluble aggregates with a small surface area available to attack. Unfortunately these features also tend to make them duller and weaker, with a degree of opacity. Another drawback with pigments is that they do not have the same colour range as dyes. By turning dyes into pigments it might be possible to overcome some of their problems without creating all of the problems of a true pigment (e.g. dullness). Many plastics already contain inorganic fillers and so putting in dyes clathrated in VPI-5 would present few problems. Such thinking has already led to a patent by Kiss *et al* [2] in which they describe the encapsulation of dyes in zeolites to form pigments.

Figure 5.1 The properties of dyes and pigments (from Gregory [1])



A possible use for dyes adsorbed into molecular sieves is as dye-delivery systems for processes such as thermal transfer printing. Presently the dye cartridges used for this have a limited lifespan due to degradation of the dyes. If the dyes could be stabilized in a molecular sieve, yet still be easily released when heated, then the process would be improved.

These then were some general ideas of the uses to which dye-filled molecular sieves could be put, the next task was to choose which dyes should be worked with.

5.2 Selection of Dyes

In view of the fact that this project was part-funded by I.C.I. plc., who at that time manufactured many dyes, it was decided to choose from their range. Dr Peter Gregory (Zeneca Specialties, Blackley (formerly ICI)) kindly supplied a considerable list of some typical solvent-soluble dyes of various chemical classes. There was a high level of interest in 'chromic materials, that is dyes whose colour was affected by their environment, e.g. thermochromic dyes, which changed colour at set temperatures, or solvatochromic dyes whose colour was affected by solvents. Some of the dyes listed showed thermochromicity. The dyes to be chosen were not only to be used with VPI-5 but, as will be seen in the next chapter, some were also to be used with faujasite-type structures and so amongst the criteria used to choose them was a range of molecular sizes. Size was also likely to affect the way in which different dyes interacted with VPI-5: large dyes being forced to interact more strongly.

Another important factor was that the chosen dyes covered a range of chemical classes, this not only gave different functional groups, but also meant that the shapes of the dyes were very different, something which could affect interactions with molecular sieves. The final feature used to help draw up a shortlist of dyes was whether or not they could be supplied as reasonably pure samples of a single molecular type, (many commercial dyes are either mixtures or cannot be easily produced to good purity).

Next, the list of possible dyes had to be whittled down to a manageable number. The way in which this was first done was by the use of scale models. It consisted of making models of the various dyes by use of a Catalin modeling kit, putting these into what was thought to be their optimum configuration and seeing if the molecules could enter models of VPI-5 pores or faujasite cages which were made to the same scale (1cm to 1Å).

Later on there was an opportunity to do some computer based molecular modeling work with Dr P. Cox (then ICI, now University of Portsmouth) at ICI Wilton. The dyes were built up and energy minimised to produce their optimum spatial arrangements. They were then boxed, that is the computer worked out what was the smallest possible box into which the dye in its optimum arrangement would fit. Figure 5.2 shows some of the molecules created by this technique. The dimensions of the molecules could then be compared to the pore openings of VPI-5 or faujasite to see if the dyes could fit in. In this way a number of borderline dyes (as chosen by the physical models) were either kept or rejected. The sizes of the chosen dyes are listed in Table 5.1 at the end of this section.

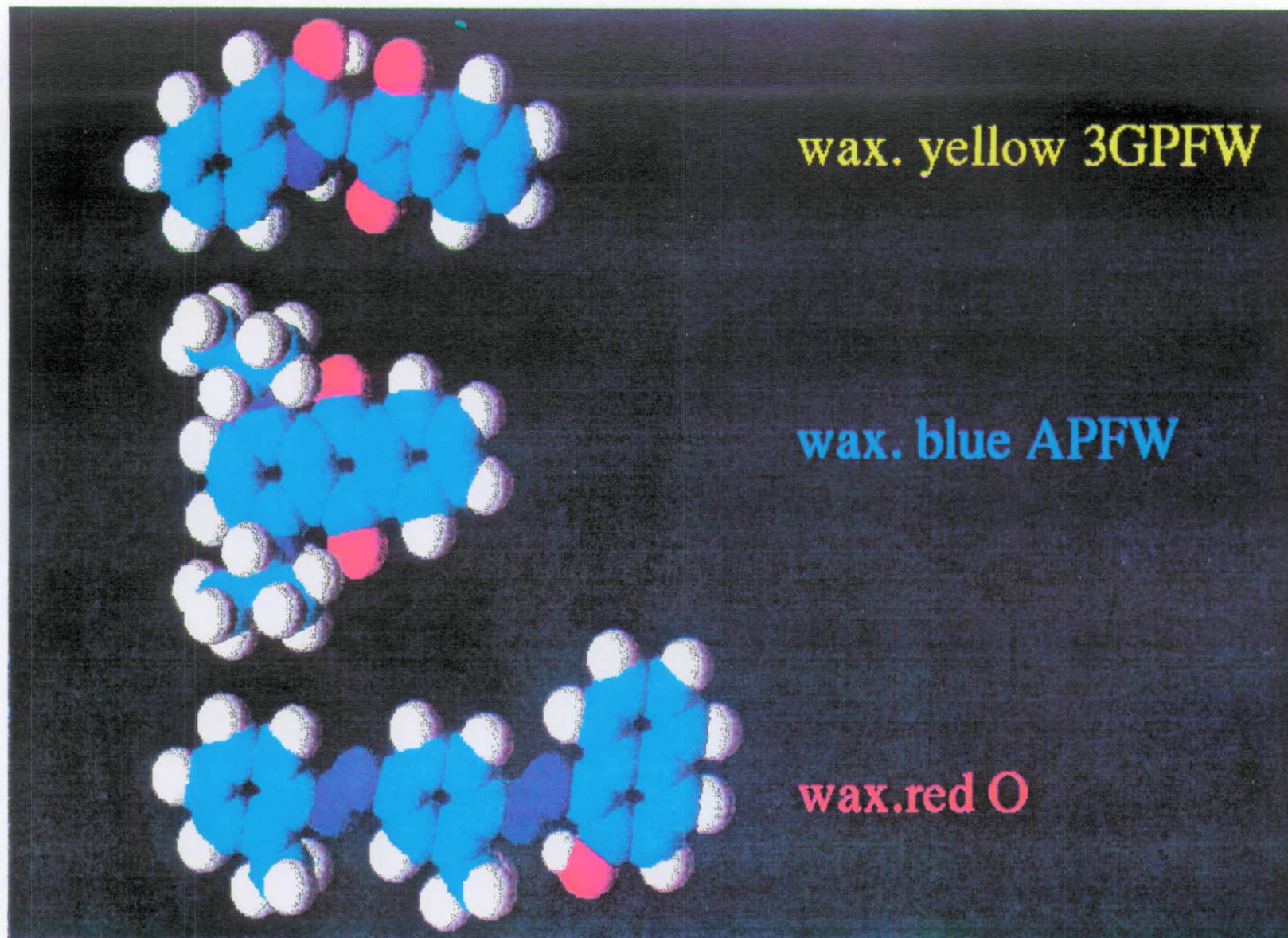
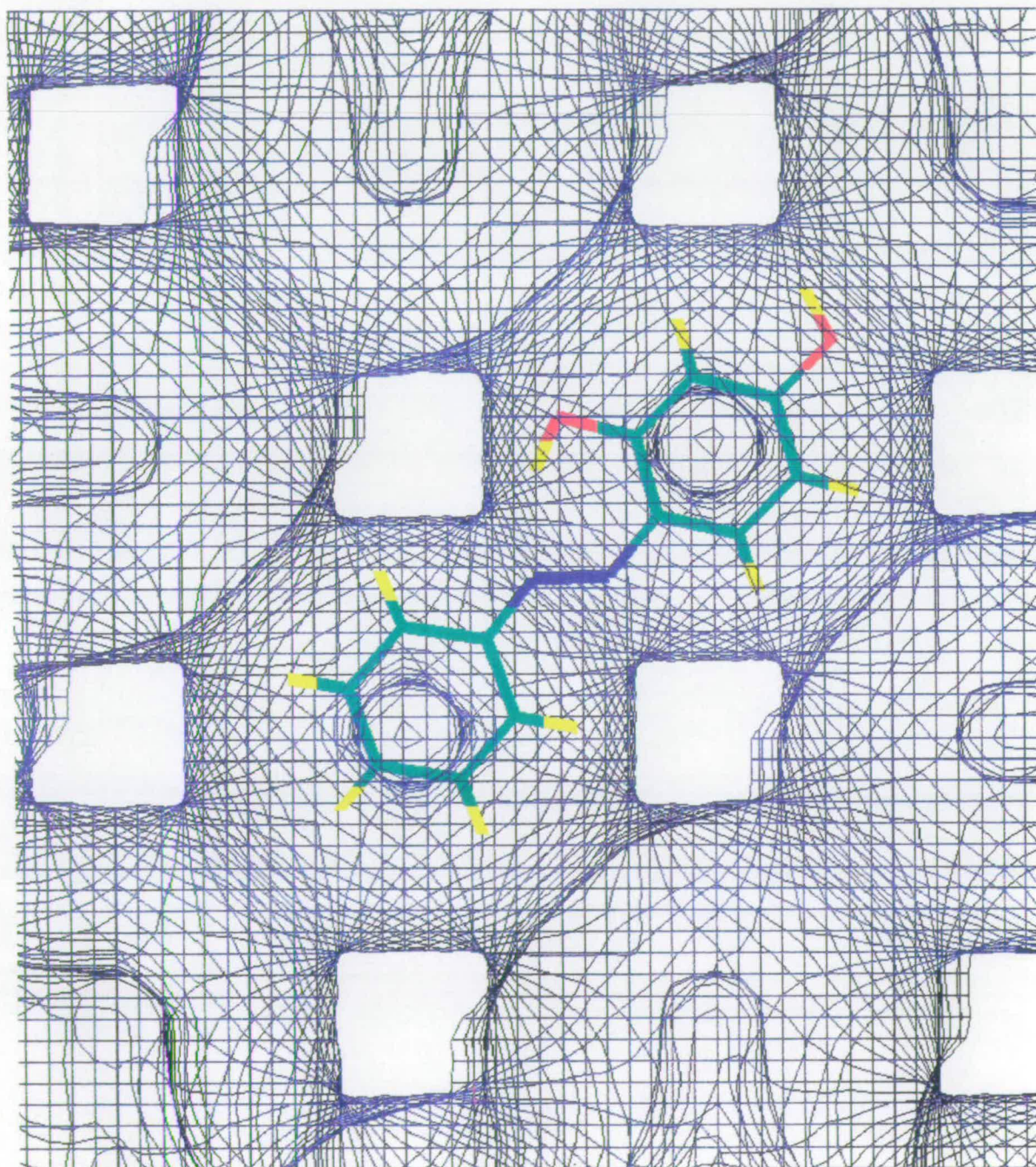


Figure 5.2 The structures of some dye molecules modelled by computer

That computer technique was a further version of the physical modeling which had been done, although the ability to energy minimise the molecules gave it added accuracy. A better technique was to create dehydrated molecular sieve frameworks and map the internal void space. It was then possible to see if the dyes would fit into this space. Figure 5.3 shows such a map, created for faujasite, with a dye molecule superimposed, whilst Figure 5.4 shows some dye molecules fitted into the pores of VPI-5.

Although this chapter is concerned solely with the sorption of dyes into VPI-5, the modeling concerned dyes for both VPI-5 and faujasite and so it seems relevant to mention here the final modeling technique which was used, but only for faujasite. Dyes were moved through the framework in steps of 1\AA with energy minimisation at each step. This gave an idea of how easy or difficult it was going to be for the dyes to move through the faujasite framework. Figure 5.5 shows the energies of several molecules and Figure 5.6 shows some of the steps of a molecule moving through the framework (note that the channel along which the dye is moving lies in the plane of the page and at right angles to those channels whose pores can be seen). For the sake of clarity only every ninth step is shown, however the figure gives a good impression of how the dye molecule moves along a channel.

Figure 5.3 A map of the internal void space of faujasite



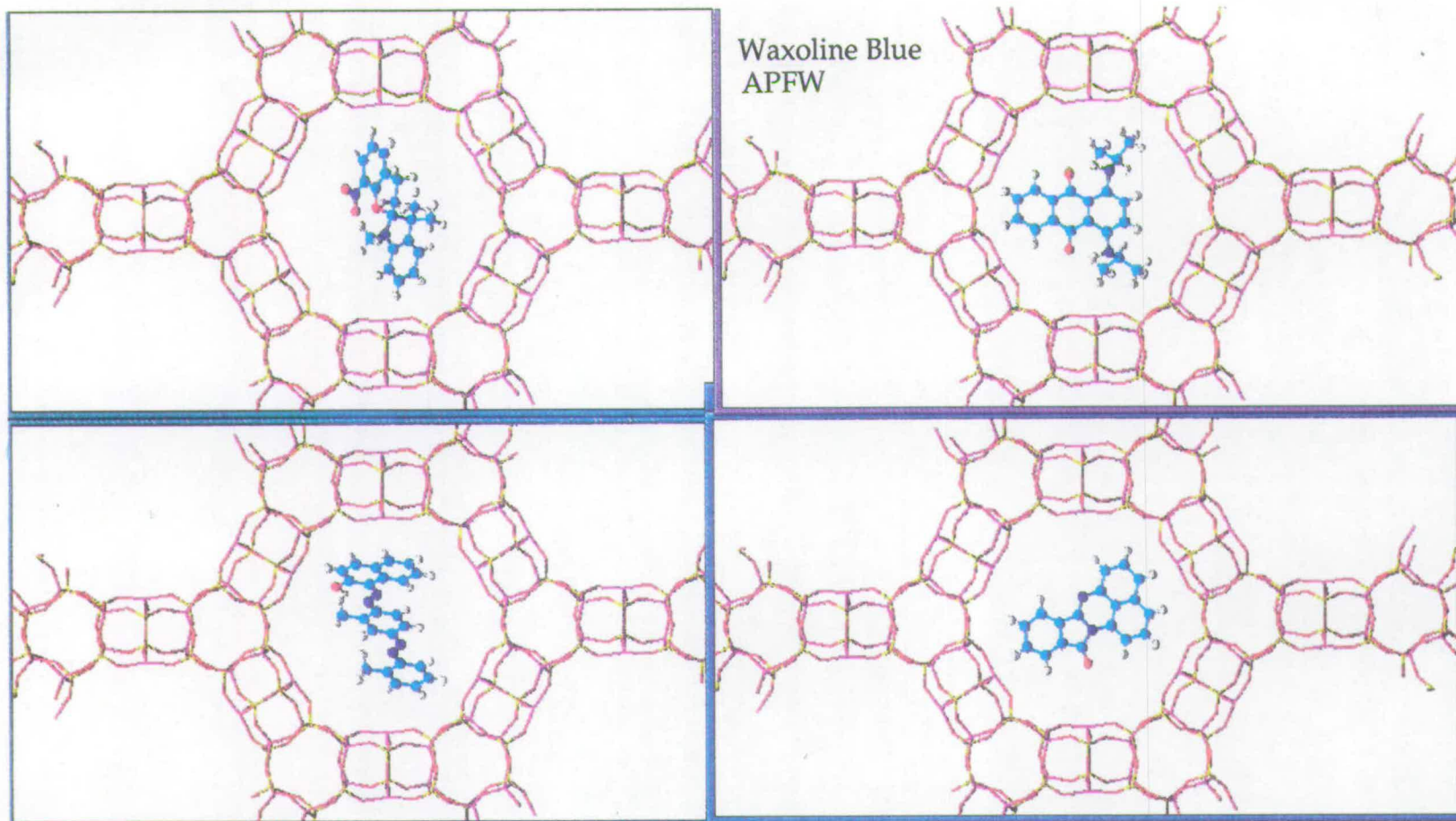
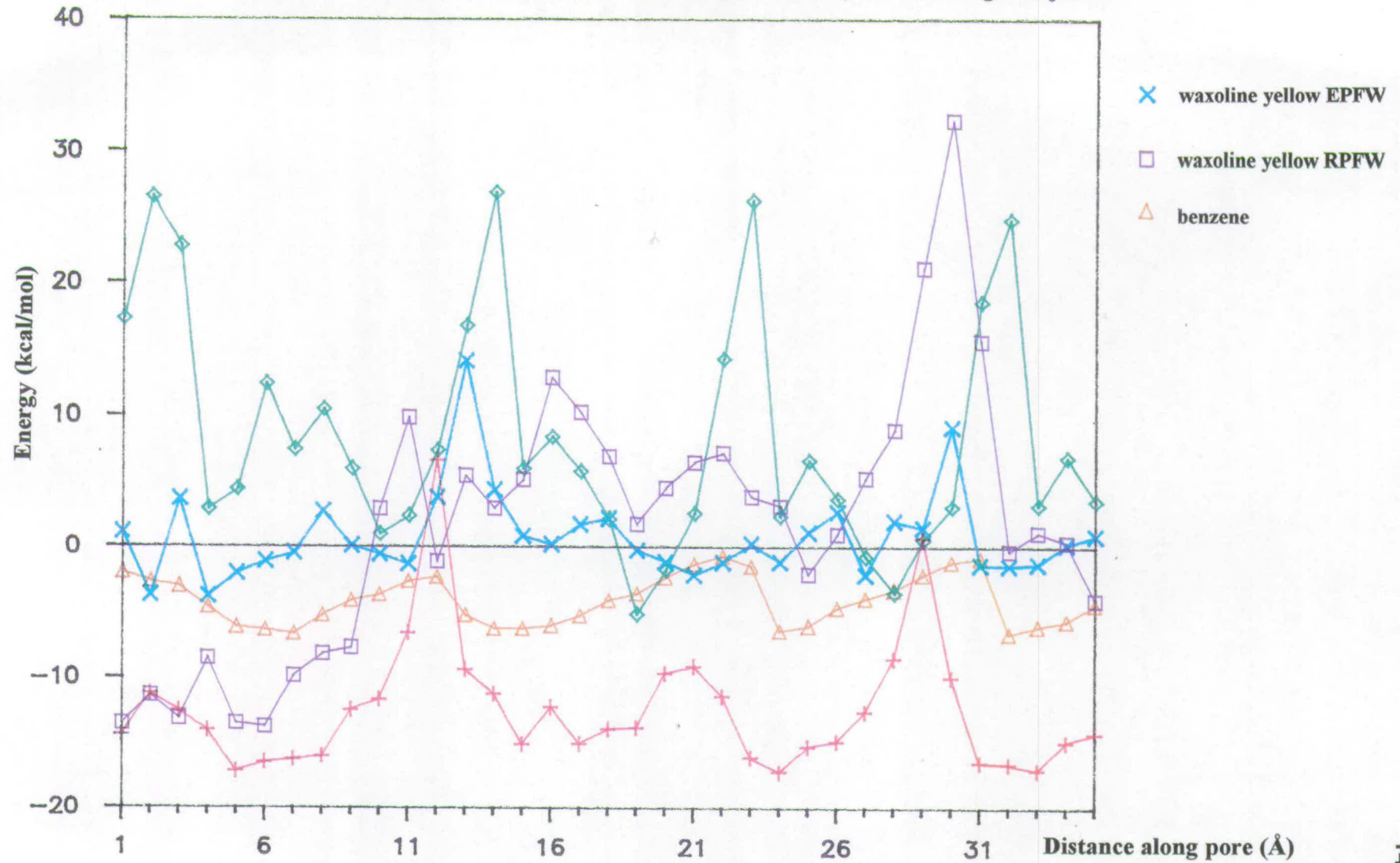


Figure 5.4 Some dye molecules fitted into the pores of VPI-5

Figure 5.5 The energy of dye molecules as they move through faujasite



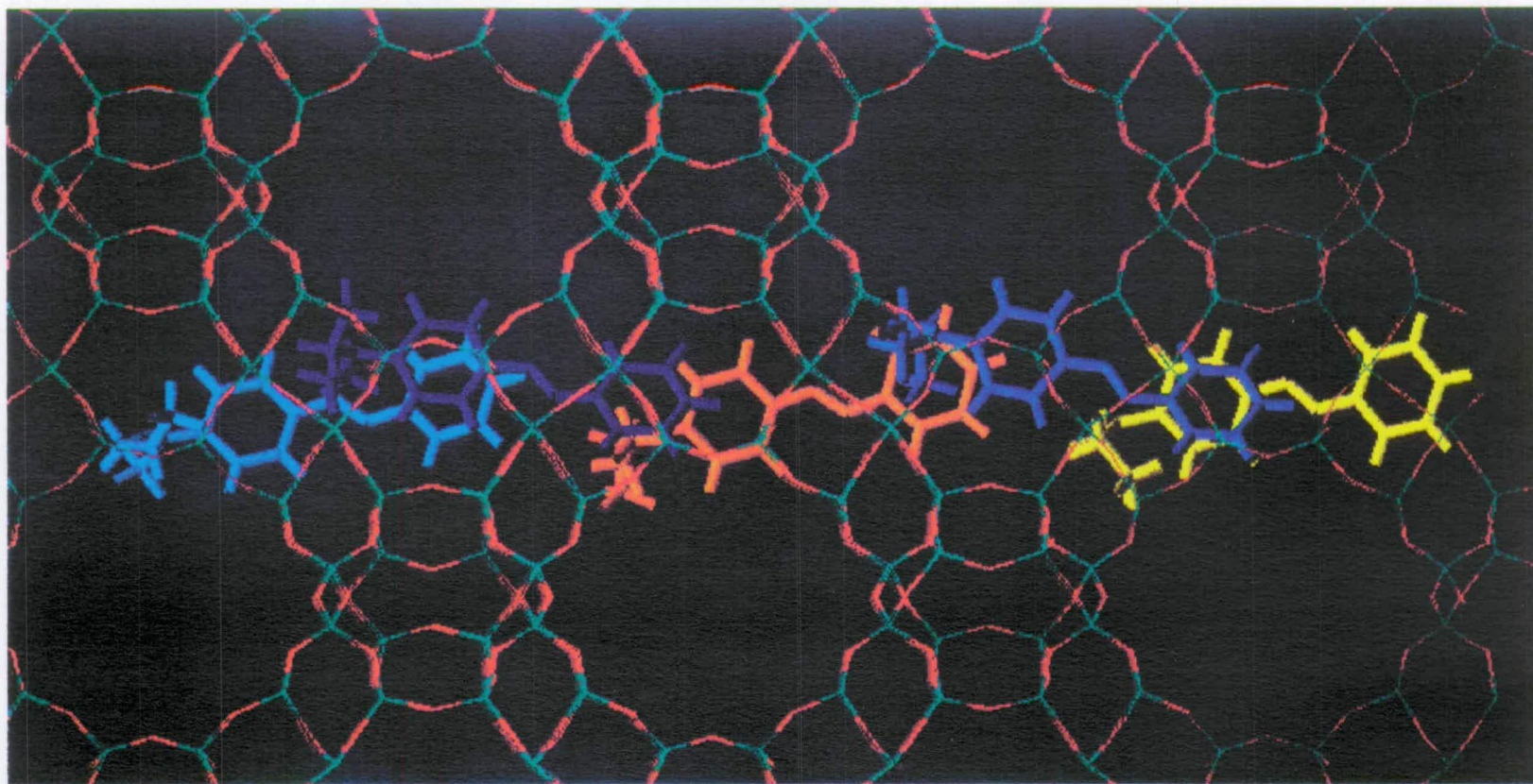


Figure 5.6 The movement of waxoline yellow EPFW through faujasite

After all of this, a total of nine dyes were selected for use with VPI-5. As desired they covered a range of sizes and chemical classes. Two of them were thermochromic, that is at specific temperatures they underwent a colour change. The dyes and their structures are listed in Figure 5.7. Table 5.1 lists the maximum sizes of some of the dyes in each of the three dimensions, *i.e.* what size box they would fit into. These data were used to calculate the volumes occupied by the molecules. The volumes were used to calculate the maximum number of dye molecules which could be accommodated per unit cell of VPI-5, in the 12Å channels only, and from that the maximum dye-loadings as %w/w. The calculations used the following additional data:

Davis *et al* [3] reported that VPI-5 had an aluminophosphate framework density of 2.60 g cm⁻³, 36 TO₂ per unit cell, and a pore volume of 0.255 cm³ g⁻¹ for the unidimensional pores. Rudolf and Crowder [4] reported that the volume of a unit cell of VPI-5 was 2531.4 Å³.

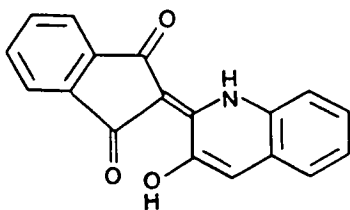
From these the number of unit cells per gram of dry VPI-5 was calculated as 2.48×10^{20} and hence 1.86×10^{20} for VPI-5 with a water content of 25% w/w. Also calculated was the pore volume of each unit cell, at 1.68×10^{-21} cm³.

The number of dye molecules which could fit into each unit cell was found to be between 1 and 3, which corresponded to maximum loadings of around 10 % w/w.

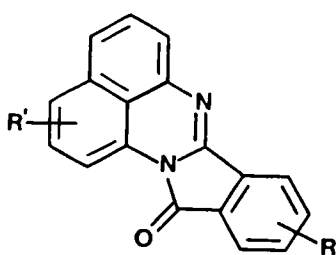
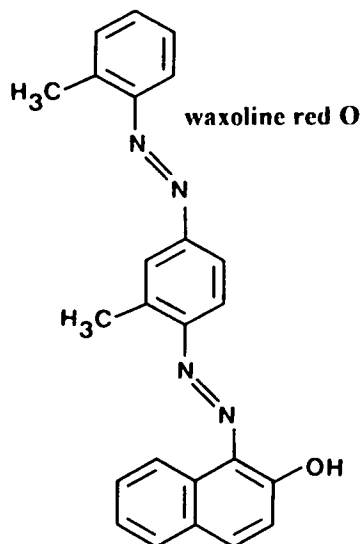
Table 5.1 The sizes of chosen dyes

Dye	Size (Å)		
	x	y	z
Dispersol yellow C-5GN	16.82	11.76	8.19
H113471	13.10	9.21	8.71
Waxoline orange 3GPFW	13.31	9.29	4.14
Waxoline blue APFW	12.27	13.06	6.42
Waxoline red O	20.28	9.89	4.25
Waxoline yellow 3GPFW	15.33	8.38	3.62
Waxoline yellow EPFW	15.94	7.25	7.52

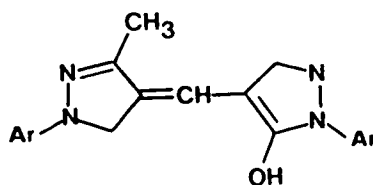
Figure 5.7 Structures of the dyes used with VPI-5



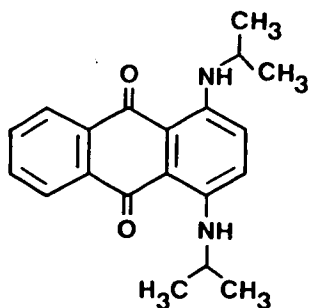
waxoline yellow 3GPFW



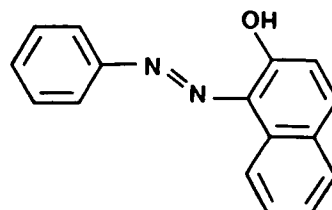
waxoline orange 3GPFW



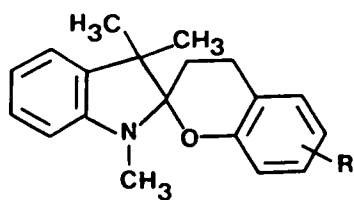
waxoline yellow 2GPFW



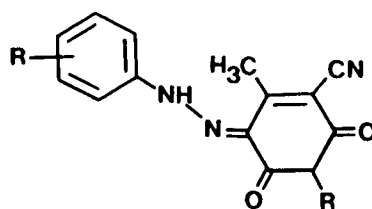
waxoline blue APFW



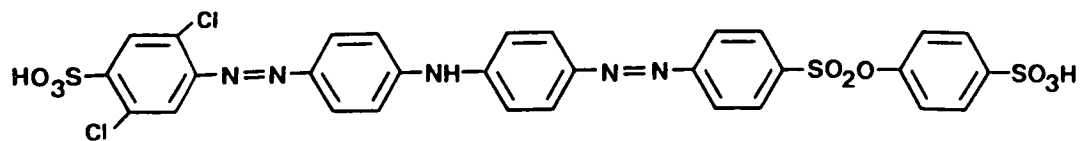
waxoline orange EPFW



H113471



dispersol yellow C-5GN



H104479

All of the dyes listed in Table 5.1, with the exception of H113471, belong to classes of dye which Gregory [1] considered to be the most suitable dyes for use in thermal transfer printing.

A problem with the use of VPI-5 was that it has a polar hydrophilic structure and its channels are normally full of water, whilst the dyes which were to be used were insoluble in water. The approaches which were considered for sorption were:

i) To create an intimate physical mixture of dye and VPI-5 and to then dehydrate the VPI-5 in order to encourage sorption on dye.

ii) To look for a solvent which could carry the dyes into VPI-5, preferably one which would be relatively easy to remove afterwards, without desorption of dye.

The initial approach was to screen a variety of techniques which utilised these two approaches. From the results of those experiments further work evolved which built upon what had been learned. Thus the work in this chapter describes the chronological development of a successful method for loading VPI-5 with dye.

5.3 Dehydration of physical mixtures of VPI-5 and Dye.

Seven dyes were available initially, they were:

Waxoline red O

Waxoline blue APFW

Waxoline yellow 2GPFW

Waxoline yellow 3GPFW

Waxoline orange 3GPFW

Dispersol yellow C-5GN

H113471

Later the dyes H104479 and waxoline *orange* EPFW became available.

5.3.1 Initial Work.

Experimental

Mixtures of VPI-5 and each of the dyes were made by thoroughly grinding 10% w/w dye with VPI-5 in an agate mortar. Agate was used because dyes did not readily adhere to it and it was easy to clean, to prevent cross-contamination of dyes. Each mixture was split into three parts which were treated as follows:

One part was kept for reference.

One part was put into an open glass vial and heated at 95°C for 16 hours.

The final part was put into an open glass vial and stored in an evacuated desiccator, over P_2O_5 , for six weeks at room temperature.

The two different methods of dehydrating VPI-5 were chosen for their contrasting conditions. It was known that VPI-5 would transform to $AlPO_4-8$ at 95°C, but it was hoped that the dyes would be mobile enough at that temperature to enter the pores, prior to transformation. At this stage of the project it was thought that VPI-5 would not transform to $AlPO_4-8$ at room temperature. Therefore, although the dyes were likely to have very low mobility at that temperature, it was hoped that low pressure and the gentle dehydration of VPI-5 would encourage their sorption.

Samples were examined visually and by a variety of techniques which included thermal analysis, XRPD, IR, Raman, and UV/vis spectroscopy.

In order to assess whether dye was trapped within transformed structures the analyses were done before and after thorough washes with ethanol to remove excess dye. The method used was to place a sample in a test tube with ethanol. This was ultrasonically shaken for 10 minutes. The solids were allowed to settle and the ethanol decanted off and replaced with fresh ethanol. The process was repeated until the ethanol ceased to take up any colour from the crystals.

Also analysed were blanks of dye only, dye mixed with alumina and heated, and in some cases dye mixed with $AlPO_4-8$ and heated. From all of this a wealth of information was generated, not only on the samples themselves, but also on how useful the analytical techniques were likely to be.

Results

The first thing to be noticed about samples of dye and VPI-5 that had been heated at 95°C was that many of them were different in colour to their unheated physical mixtures. They were also different in colour to pure dyes or samples of dye and alumina which had also been heated at 95°C. This feature was not so noticeable in most of the samples of dye and VPI-5 which had been dried in an evacuated desiccator.

Much work concentrated on trying to quantify the colour changes which had taken place, using KBr discs for visible spectroscopy, as described in chapter 2. Unfortunately it proved impossible in most cases to detect any changes in the visible spectra of dye/VPI-5 complexes compared with the spectra of dye on alumina or of pure dye. The collection of spectra was hampered by light scattering by the various inorganics involved, the VPI-5, KBr, and alumina. Thus the only record of apparent colour changes are the visual descriptions set out below in Table 5.2.

Lack of good spectra meant that it was not possible to tell whether the colour changes had arisen from changes to the physical form of the particles of dye rather than through interaction with VPI-5. Much of the colour of dyes and pigments is from reflected light and the nature of this is affected by the physical form of the dye particles or substrate. Therefore if heating had caused dye to cease existing as particles and to coat VPI-5 crystals then a colour change could be seen without there having to be a strong interaction between the two materials. Some of the changes were however so striking that interactions are strongly suspected.

By looking at the colours of the washed samples however the table did give good evidence that for most of the samples which were heated to 95°C there was some amount^{of} dye trapped inside VPI-5. The evidence was that most of the heated samples remained strongly coloured whilst the desiccated samples did not.

Thus it had not been possible to remove all of the dye from most of the heated samples, which indicated the presence of trapped dye.

Table 5.2 Colours of the samples as determined by visual examination.

Dye	Pure dye only	Dye ground with alumina and heated to 95°C for 16 hr	Dye ground with VPI-5 and heated to 95°C for 16 hr	Dye ground with VPI-5 and dried in an evacuated desiccator
Waxoline yellow 2GPFW	a	Orange-yellow	Pale yellow	Orange-yellow
	b		Very pale yellow	Very pale yellow
Waxoline yellow 3GPFW	a	Orange-yellow	Orange-yellow	Orange-yellow
	b		Orange-yellow	Pale yellow
Waxoline orange 3GPFW	a	Dark orange	Light orange	Dull orange-brown
	b		Orange	Pale orange
Waxoline red O	a	Very dark red	Dull brown-red	Burgundy
	b		Burgundy	Dark purple
Waxoline blue APFW	a	Very dark blue	Dull grey-blue	Burgundy
	b		Dark blue	Pale purple
Dispersol yellow C-5GN	a	Dull yellow	Dull yellow	Dark blue
	b		Bright yellow	Dark blue
H113471	a	Buff	Buff	Pale blue
	b		Orange	Pale blue
	a		Orange	Yellow
	b		Orange	Pale yellow

^a Unwashed sample^b Washed sample

To check that the remaining colour of the heated VPI-5 samples was not merely due to a heat induced reaction between the dyes and the AlPO_4 framework, some of the dyes were heated with AlPO_4 -8 made from the same VPI-5. The temperature was again 95°C and the time 16 hours. This time all of the dyes could be washed off to leave virtually white AlPO_4 -8. Therefore dyes which could not be washed from the heated VPI-5 were not chemisorbed onto the exterior through the effects of heat, but were trapped inside the collapsed structure.

IR spectra were also recorded for all of the samples, to see if they could show up any interactions between the dyes and VPI-5. Unfortunately the VPI-5 absorptions swamped any dye signals and no useful information could be gained.

XRPD showed that all of the samples, whether heated or kept in a desiccator, had very little or no VPI-5 left. For the desiccated samples this was a very surprising result as no $\text{AlPO}_4\cdot 8$ had been expected to form at room temperature. This gave further evidence that E_A for the transformation of VPI-5 to $\text{AlPO}_4\cdot 8$ was very low. Estimates are given in Table 5.3 of the amount of conversion to $\text{AlPO}_4\cdot 8$ which had taken place in each of the samples.

Table 5.3 Degree of conversion to $\text{AlPO}_4\cdot 8$ in heated and desiccated samples of mixtures of VPI-5 and dye.

Dye	Sample heated at 95°C overnight	Sample stored in evacuated desiccator over P_2O_5 (6 weeks, room temp.)
Waxoline yellow 2GPFW	100%	94%
H113471	100%	92%
Waxoline yellow 3GPFW	100%	90%
Dispersol yellow C-5GN	96%	82%
Waxoline orange 3GPFW	94%	92%
Waxoline red O	86%	83%
Waxoline blue APFW	72%	82%

Thermal analysis on samples which had been washed clean of excess surface dye gave more information with which to interpret these results. Analysis of the traces suggested that the amount of sorbed dye was negligible in all cases except where waxoline blue APFW and waxoline red O had been heated to 95°C with VPI-5. The TGA curve of washed 95°C VPI-5 and waxoline red O showed about 0.5% weight loss attributable to dye, whilst for waxoline blue APFW the amount was 1%. Thus there was definitely sorption and entrapment of these dyes.

It is interesting to note that all of the other samples which had been heated at 95°C did not contain enough trapped dye to be measurable with the TGA equipment which was used. In fact their TGA curves were almost exactly the same shape as those which

were produced by their equivalent desiccated samples, this despite the fact that most of the washed 95°C samples were fairly strongly coloured, whilst the washed desiccated ones were not (see table 5.3). Thus it was shown that it took very little trapped dye to cause strong colouration of VPI-5.

For all the other dyes the TGA curves of the washed 95°C samples and the washed desiccated samples followed each other very closely. The lack of colour of the desiccated samples showed that they contained very little dye, therefore very little of the weight loss shown on their TGA curves was attributable to dye. This suggested that, despite fairly strong colouration in the 95°C samples (see Table 5.4) most of them did not in fact contain much trapped dye, since their TGA curves were not noticeably different from those of the lightly coloured desiccated samples.

The combination of XRPD and TGA results suggested that waxoline red O and waxoline blue APFW had a stabilising effect upon the VPI-5 framework in those samples which were heated to 95°C. It was remarkable just how much stability there was, considering the small quantities of the two dyes which were trapped. Waxoline blue APFW was clearly the most effective dye at prevention of the transformation of the VPI-5 framework to $\text{AlPO}_4\text{-8}$ and that fitted in well with its higher loading. It was also noted that waxoline blue APFW was the dye whose size most closely matched that of the VPI-5 channels.

All stabilisation in heated samples could be attributed to dye since it had been shown (Table 5.3) that the heating conditions could cause 100 % transformation to $\text{AlPO}_4\text{-8}$. Thus the unquantifiable amounts of waxoline orange 3GPFW and dispersol yellow C-5GN trapped inside VPI-5 had slight stabilising effects.

The desiccated samples showed less $\text{AlPO}_4\text{-8}$ formation than the heated samples, however this is attributed mainly to incomplete transformation due to mild conditions, rather than to stabilisation of VPI-5 by dye. The variation between the desiccated samples in the amount of $\text{AlPO}_4\text{-8}$ which did form may have been due to small amounts of dye which did manage to enter the pores, but it could easily have been due to experimental variation. Either way, the TGA data and the pale colourations of the samples implied that none of the dyes had a high enough mobility at room temperature to penetrate far into VPI-5 crystals.

H113471. A special mention should be made of H113471, this is a thermochromic dye which undergoes a reversible colour change from buff to purple at 168°C. When heated with VPI-5 it produced an orange product which was no longer thermochromic. Yet the pure dye could be recovered unchanged from these samples, with its thermochromicity restored. The mechanism by which H113471 changes colour is a conformational change in a spiro linkage [5] and it is most likely that sorption into VPI-5 restricts the ability of the molecule to undergo the change.

5.3.2 The use of a vacuum line

Although the use of an evacuated desiccator had not been successful in enabling dye to be sorbed into VPI-5, the use of reduced pressures still had potential and so was investigated further. The next step in the search for ways in which to sorb dyes was the use of a vacuum line. It was hoped that the much lower pressure of a vacuum line could be used to aid the sorption of dye into VPI-5. Work described in chapter 4, after the work of Annen *et al* [6] and Akporiaye *et al* [7], had shown that it was possible to get controlled dehydration of VPI-5 without the formation of $\text{AlPO}_4\cdot 8$. A very low pressure might also mobilise dye so that it would enter the dehydrated pores.

Experimental For this work only waxoline blue APFW was used because of its good results described in 5.3.1, of highest dye-loading and greatest amount of stability conferred upon the VPI-5 framework. Initially the line was set up so that the dye sat in a finger below the VPI-5, this was to enable dye to be heated if necessary, without heating the VPI-5.

Further work was done with intimate physical mixtures of dye and VPI-5, so that the organic had only to move a short distance to get into the pores. The amount of dye used was 10% w/w. A number of attempts were made to load dye, some done at room temperature, others heated to up to 80°C, although always after an initial period of evacuation at room temperature, since this was stated in the references to be essential to successful dehydration.

Samples produced in the vacuum line were analysed by XRPD and thermal analysis and, if there was no $\text{AlPO}_4\cdot 8$ formation when they were removed from the vacuum line, their thermal stability was investigated.

Results. It certainly proved possible to evacuate and heat mixtures of VPI-5 and waxoline blue APFW without any $\text{AlPO}_4\text{-8}$ formation. The method did not however prove very successful at causing dye to be sorbed into VPI-5. On the first attempt dye and VPI-5 were evacuated for 16 hours without any sign of the dye moving. Heat was then applied, taking the dye to 80°C , but after seven hours the dye had only moved a short distance, not far enough to reach the VPI-5. It was after this that intimate physical mixtures were used.

Table 5.5 details the amounts of $\text{AlPO}_4\text{-8}$ formed when various evacuated samples, which had been equilibrated in air, were heated to 900°C . It should be noted that the VPI-5 which was used in the vacuum line had been washed with hot water to improve its thermal stability.

Table 5.5 The thermal stability of evacuated samples of VPI-5 and waxoline blue APFW.

Sample conditions	% $\text{AlPO}_4\text{-8}$ after heating to 950°C
Evacuated 34h/RT	75
Evacuated 96h/RT	82
Evacuated 48h/RT, 24h/ 53°C	80
Evacuated 48h/RT, 5h/ 53°C , 24h/ 70°C	60

What can be seen from the table is that for the first three samples there was no noticeable improvement in stability above what would be expected for an untreated physical mixture. It was only the fourth sample which showed a stability gain and then not a large one. Furthermore thermal analysis did not show much difference between the evacuated samples and physical mixtures of VPI-5 and waxoline blue APFW, indicating that the amount of sorbed dye remained low in all cases.

This method of producing dye loaded samples did not seem to offer any advantages, in fact quite the opposite:

Sorption did not occur at significantly lower temperatures than other methods, thus the vapour pressures of the dyes were still very low.

There were several operational problems with the vacuum line which made it difficult to achieve the best conditions..

Therefore no further work was carried out with the vacuum line.

5.3.3 Further work on heating physical mixtures of VPI-5 and dye.

With little success gained from evacuating VPI-5 with dye, work returned to heating intimate physical mixtures of dye and VPI-5 in an ambient atmosphere. The obvious problem with this approach was that heating, although it aided the mobilisation and sorption of dye, caused the formation of $\text{AlPO}_4\text{-8}$. Therefore much work was carried out on ways in which this method could be optimised such that the rate of $\text{AlPO}_4\text{-8}$ formation was minimised and the level of dye uptake was maximised. Again, due to its performance in initial work, the development of techniques was done mainly with waxoline blue APFW. As before 10% w/w dye was used.

Experimental. For the initial work a temperature of 95°C had been chosen because it seemed to offer a suitable compromise between conflicting needs. At that stage it was thought that water might be acting as a mineralising agent in the transformation of VPI-5 to $\text{AlPO}_4\text{-8}$, therefore a high temperature was wanted in order to get rid of the water as quickly as possible. A high temperature was also required in order to maximise the mobility of the dyes. On the other hand too high a temperature might decompose some of the dyes, especially if heating was prolonged.

This problem explains why so much study of the thermal stability of VPI-5, as detailed in Chapter 4, had been undertaken. The stability studies had swiftly shown that it was only at very high temperatures that there was likely to be a benefit from rapid removal of water. At the relatively low temperature of 95°C all that happened was that the VPI-5 swiftly transformed to $\text{AlPO}_4\text{-8}$. Therefore in order to get a slower rate of $\text{AlPO}_4\text{-8}$ formation, and so allow more time for dye sorption, further physical mixtures of dye and VPI-5 were heated in open vials at a lower temperature: 80°C was chosen.

The wish to remove water as quickly as possible was also the reason why open vials had been used to heat the mixtures. This was because reference had been made by others [8] to the transformation to $\text{AlPO}_4\text{-8}$ being a 'self-steaming' process in a closed container, however work on the stability of VPI-5 heated in sealed containers, as described in Chapter 4, had shown that VPI-5 remained intact if heated in a sealed container. Therefore in an attempt to slow down the rate of water loss from VPI-5, and hence the rate of $\text{AlPO}_4\text{-8}$ formation, samples were heated in a variety of containers which gave different rates of water loss. The containers ranged from vials stoppered with permeable plastic caps through to sealed glass tubes which prevented all escape of water, a range of temperatures were used. More work with open vials

was also done, but at still lower temperatures. A wide range of heating times were used, from a few hours to ten weeks.

Samples produced by these experiments were examined by XRPD and thermal analysis. As before they were washed to remove surface dye, this time however they were soxhlet-extracted with ethanol or methylene chloride until the returning solvent ran clear.

Note that removal of all or most of the dye by washing could indicate more than just that there had been no sorption. In some cases it could show that there were still open pores through which sorbed dye could be removed. This required further evidence from other analytical techniques which will be detailed in the results section.

One attempt was made to overcome the problem of solvent from the washes entering the pores by washing a sample of VPI-5 loaded with waxoline blue APFW with a liquid detergent which it was hoped would be too large to enter the pores of VPI-5. The method used was to repeatedly shake a sample ultrasonically with detergent and water, then decant the liquid and repeat until the supernatant remained clear.

Results.

Open containers. No improvements with respect to the results in 5.3.1 were seen in samples which were heated in open vials. The lower temperatures meant that conversion to $\text{AlPO}_4\cdot 8$ took longer, but also meant that dye was less mobile and so greater loadings were not seen.

The attempt to use liquid detergent to wash away excess dye was not successful, much surface dye remained and even after several washes with water so did much detergent. Therefore the detergent had interacted with the VPI-5 and so its use was not repeated.

Sealed Containers. The next experiments investigated whether keeping VPI-5 intact but not allowing any water to escape, by heating in sealed systems, would enable dye to be sorbed. VPI-5 emerged intact from all of the sealed tubes, even ones which had been heated to 140°C . What was noticeable in most cases however was that there had been no colour change: the samples were still the same colour as physical mixtures, rather than the noticeably different shade of blue previously seen in heated mixtures of VPI-5 and waxoline blue APFW. Exceptions to this were two samples heated at 140°C for 8 and 12 days respectively. These samples had a charred appearance due to

decomposition of the dye.

Thermal analysis indicated that no dye had been sorbed into VPI-5 in any sample heated in a sealed tube. The traces looked very similar to those of unheated physical mixtures of VPI-5 and waxoline blue APFW. Similarly the thermal behaviour of the VPI-5 was the same in these samples as in unheated physical mixtures, *i.e.* total or near total transformation of VPI-5 to $\text{AlPO}_4\text{-8}$ when heated to 900°C for thermal analysis and only a small amount of VPI-5 left when heated at 80°C overnight. Also when heated overnight at 80°C the samples took on the shade of blue seen in previous heated samples where dye had been sorbed into the pores.

Thus the work with open and sealed containers had shown two things of use for the sorption of dye into VPI-5:

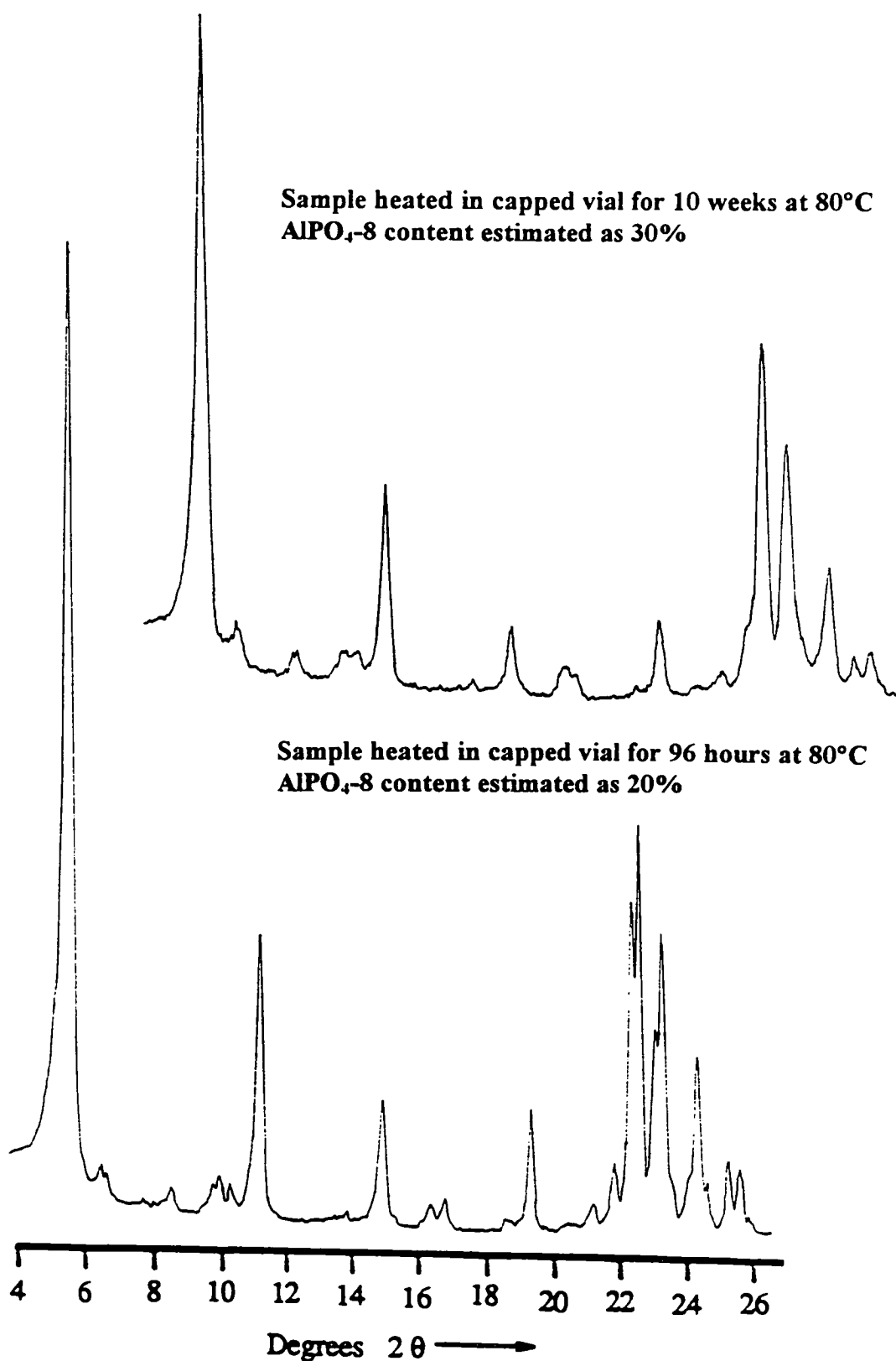
- Waxoline blue APFW (and presumably other dyes also) was not sorbed into VPI-5 unless there was some water loss from the structure.
- The colour change which had been reported in 5.3.1 was not merely due to heating the dye or heating it in the presence of VPI-5, the change in colour was attributable to sorption of dye into VPI-5.

Both of these points were probably applicable to the uptake of all of the dyes. It was also seen that 140°C was too high a temperature for waxoline blue APFW, as it decomposed.

Capped Vials. The plastic caps used to stopper these vials were shown, by simple tests, to become permeable to water when heated. This meant that these containers represented an intermediate stage between open and sealed: VPI-5 could be heated at temperatures high enough to mobilise dye, but the rate of water loss was limited so that $\text{AlPO}_4\text{-8}$ formation was very slow.

The initial sample to be heated in a capped vial was heated for 96 hr at 80°C . Examination of the contents by XRPD showed that there had been very little $\text{AlPO}_4\text{-8}$ formation, almost all of the VPI-5 appeared to be intact. In contrast a VPI-5 blank heated in a similar container had completely transformed to $\text{AlPO}_4\text{-8}$. Figure 5.8 shows the XRPD pattern of the dye containing sample, $\text{AlPO}_4\text{-8}$ content was estimated at 20%.

Figure 5.8 The XRPD patterns of VPI-5 stabilised by waxoline blue APFW



Investigation of the thermal stability of the sample showed that further heating at 80°C for 24hr in an open vial did not lead to a noticeable increase in $\text{AlPO}_4\text{-8}$ content. Thus the framework had been stabilised against further change.

The sample remained strongly coloured after washing to remove free dye. However, once washed, the thermal stability of the VPI-5 structure was lost, samples heated to 80°C overnight were almost completely transformed to $\text{AlPO}_4\text{-8}$. Thermal analysis of the washed sample showed that there remained less than 0.5% dye

These results were interesting because they not only showed that much dye had been sorbed into VPI-5, but also implied that it was possible to wash out much of the dye which had supported the framework, therefore the pores had not been extensively blocked. The implication of this was that $\text{AlPO}_4\text{-8}$ formation had not started at the outside of the crystals as usual [9]. Intuitively that would be expected since the pore openings are the first point of contact for dye and would therefore be most likely to be stabilised.

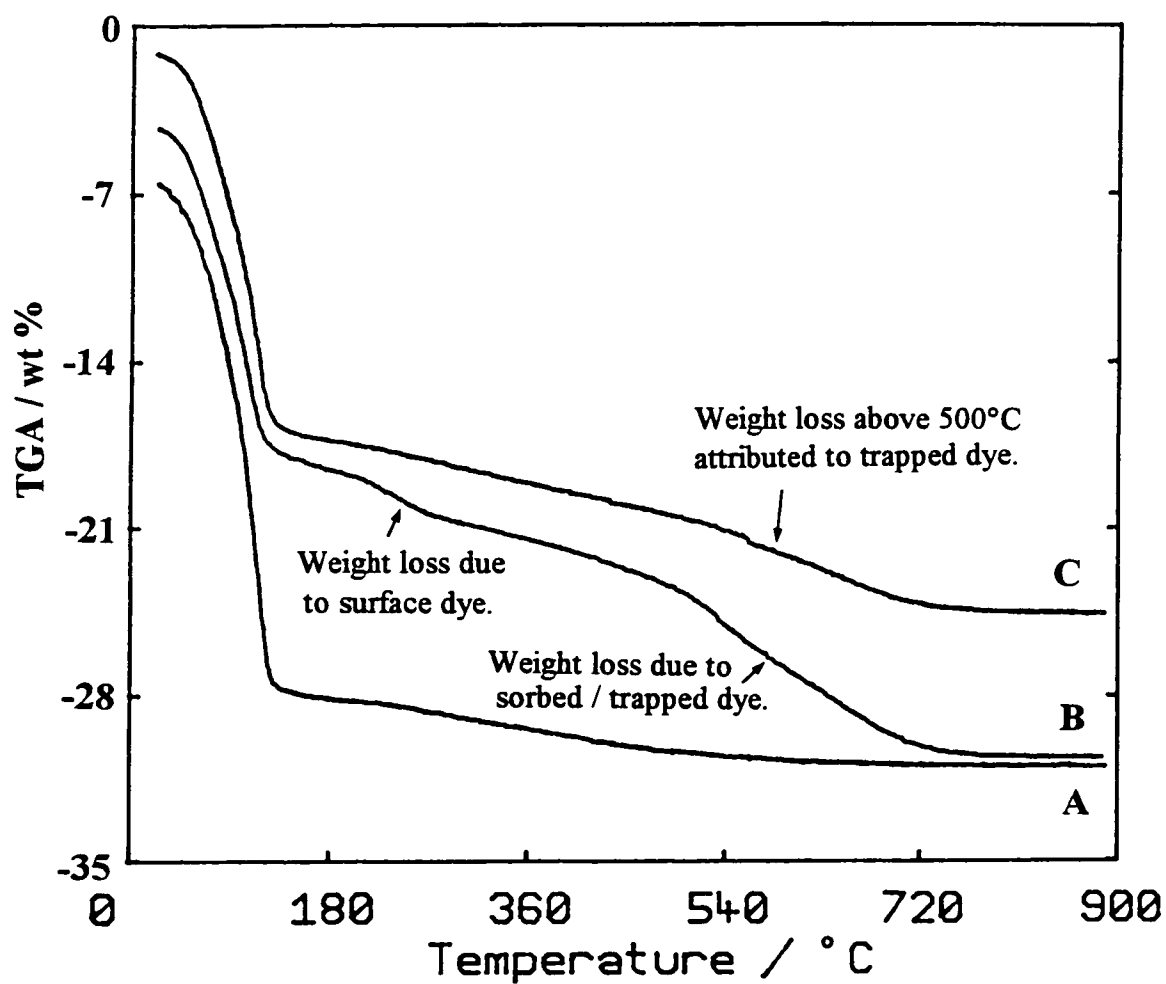
A further sample of VPI-5 and waxoline blue APFW was left in a capped vial at 80°C for ten weeks. The $\text{AlPO}_4\text{-8}$ content of this sample was estimated to be around 30%, still a reasonably low amount. Figure 5.8 shows the XRPD pattern of this sample also. It should be noted just how small the $\text{AlPO}_4\text{-8}$ peaks are, despite representing nearly a third of the crystalline material. They emphasise how much caution was required when determining how much $\text{AlPO}_4\text{-8}$ was present in samples.

Some aspects of the thermal stability of this sample were studied also.

- It was found that no more $\text{AlPO}_4\text{-8}$ was formed when the sample was heated at relatively low temperatures (up to 150°C) for short times.
- When the sample was heated to greater than 900°C the amount of $\text{AlPO}_4\text{-8}$ rose to approximately 40%.
- There was lessening of the thermal stability in samples which had been thoroughly washed, either with methanol or methylene chloride.

These results indicated that this time the dye which was responsible for the increased thermal stability of the VPI-5 framework in this sample was trapped, therefore pore blockage had occurred at the crystal exteriors. The amount of trapped dye was estimated by thermal analysis to be about 4% w/w. This was a considerable loading, equivalent to greater than 0.7 molecules per unit cell. Figure 5.9 shows the thermal analyses.

Figure 5.9 Thermal analysis traces showing waxoline blue APFW trapped within a partially transformed VPI-5 framework.



A. VPI-5 blank

B. Mixture of VPI-5 and waxoline blue APFW heated at 80°C for ten weeks.

C. Sample B soxhlet extracted with methylene chloride.

One other sample of VPI-5 and waxoline blue APFW was prepared in a capped 8ml vial, this time heated for three weeks. The $\text{AlPO}_4\text{-8}$ content upon removal from the oven was approximately 25%. Like the second sample, this level was maintained whenever the sample was heated at low temperatures, but rose when the sample was heated to 900°C , to about 35-40%. Again washing with ethanol or methylene chloride did not affect how much $\text{AlPO}_4\text{-8}$ was formed, thus indicating that the sorbed dye was trapped.

In both the second and third attempts to produce stabilised VPI-5 the vials had been opened up several times in the first few days of heating. This had been to take out small samples for XRPD analysis in order to check progress. It is thought that by releasing water vapour the samplings may have been the cause of the external collapse which had trapped sorbed dye inside the VPI-5 in both cases.

Some other attempts to use this method of capped vials to create stabilised VPI-5 complexes failed, generally because the caps of the vials popped off and so the VPI-5 rapidly dehydrated and converted to $\text{AlPO}_4\text{-8}$, thus the method was not wholly reliable.

Discussion. The results showed that heating samples in capped vials gave the best dye uptake of any of the methods tried so far, and also led to much stabilisation of the VPI-5 framework. This proved that the slow loss of water was a requirement of the process of dye sorption into VPI-5.

The enhanced stability was attributed to a high loading of dye which was able to act as some sort of structural scaffold inside the channels of VPI-5, thereby preventing collapse to $\text{AlPO}_4\text{-8}$ when water was removed. Although waxoline blue APFW was a very close fit to the channel size of VPI-5, it is not thought to have acted as a cork - preventing collapse by stopping water from escaping from the pores. The evidence for this came from thermal analysis (Fig. 5.9) which showed that water was lost from stabilised VPI-5 at similar temperatures to unstabilised VPI-5.

There were however two problems with the use of capped vials:

i) Even the most successful attempt, the first one, in which VPI-5 had been greatly stabilised and most of the sorbed dye was not trapped, still contained about 20% $\text{AlPO}_4\text{-8}$. This was taken to indicate that there was still room for more dye to be sorbed. Despite a number of attempts the result could not be bettered.

ii) The use of capped vials was not wholly reliable and so it was not possible to lay down set conditions.

Thus the next step in the heating of physical mixtures of VPI-5 and dye was to look for a method by which dehydration could be achieved in a more controlled manner. The work is described in section 5.5.

5.4 Use of Solvents to load VPI-5 with dye.

Running in parallel with the work described in section 5.3 was a programme designed to look at the uptake of dyes into VPI-5 from solvents. This work had the potential advantage of producing products which were not heavily contaminated with surface dye and which therefore did not need extensive washing.

5.4.1 Initial work.

The requirement for solvents were:

An affinity for the dyes, yet to be relatively polar in order to be attracted to VPI-5.

A low boiling point to aid removal after dye sorption.

In order to try and meet these requirements the first solvents to be used were ethanol and acetone. As was described in Chapter 4, the stability of VPI-5 to hot ethanol and acetone had been established.

Experimental

The first approach was to contact VPI-5 with solutions of dye. Not all of the dyes were used for this work: four were chosen which gave a spread of sizes from waxoline yellow 3GPFW, the smallest, through medium-sized waxoline orange 3GPFW, to waxoline blue APFW and dispersol yellow C-5GN which were at the upper limits of size for fitting into VPI-5.

The methods used in this work were:

- i) To heat VPI-5 in refluxing solutions of dye, either in ethanol or acetone.

ii) To pre-treat the VPI-5 before it was contacted with dye solutions. Here the VPI-5 was placed in a flask with some pellets of dry zeolite 3A and the relevant solvent, either ethanol or acetone. A reflux condenser was attached and the solvent was boiled vigorously for several hours. The aim was to get solvent to replace some of the pore water in the hope that this would assist sorption of dye. Zeolite 3A pellets were present to sorb water. Solvent-loaded VPI-5 was quickly filtered off from the hot solvent and transferred to a freshly made solution of dye in dry solvent. This too was heated at reflux temperature for several hours, before the VPI-5 was filtered off and washed with a small amount of dry solvent.

iii) Further attempts to get dye sorbed into VPI-5 involved the evaporation to dryness of solutions of dye in acetone and also in methylene chloride, which fulfilled the solvent requirements. Evaporation was achieved by heating and by standing at room temperature. Some of the unheated mixtures were ultrasonically shaken until nearly dry.

Samples were analysed visually, by XRPD, and by thermal analysis. Some also had their thermal stability investigated.

Results

Sorption from hot solutions of dye. After standing in hot solutions of dye in ethanol or acetone, the filtered VPI-5 showed little or no uptake of colour. Washes with cold solvent easily removed what colour there was, which suggested that the dyes were not strongly held and possibly not inside the structure. XRPD analysis showed the VPI-5 structure to be intact after filtration, but any heating in air of the material led to $\text{AlPO}_4\cdot 8$ formation. There was no gain in thermal stability of the VPI-5 treated in this way.

Pre-treatment of the VPI-5 with solvent. When the above work was repeated with VPI-5 which had been previously boiled in ethanol or acetone, to try and get solvent into the pores, the results were little better.

In one case, using waxoline orange 3GPFW in dry ethanol, the filtered solids contained discreet white and orange particles. This sample was carefully examined, to give the following results:

- XRPD analysis showed large peaks attributable to crystalline dye.
- The colour was easily washed out of the sample.

- When the sample was heated to 95°C overnight it became uniformly orange and there was complete transformation of VPI-5 to $\text{AlPO}_4\cdot 8\text{H}_2\text{O}$. Washing was now not able to remove all of the dye, the sample remained a uniform very light orange, which indicated that some dye was trapped inside the collapsed structure.

It was concluded from these findings that there had been no uptake of dye from solution. Instead, evaporation of solvent during heating led to the precipitation of dye from its saturated solution and hence to orange particles. Thus the discreetly coloured orange or white particles were crystals of orange dye and the white VPI-5, they did not arise because dye was able to get into some crystals of VPI-5 and not others.

Total collapse of the structure to $\text{AlPO}_4\cdot 8\text{H}_2\text{O}$ was another indication that no dye had entered the VPI-5 from solvent, although as would be expected (from 5.3.1) during heating a small amount of dye did enter the pores.

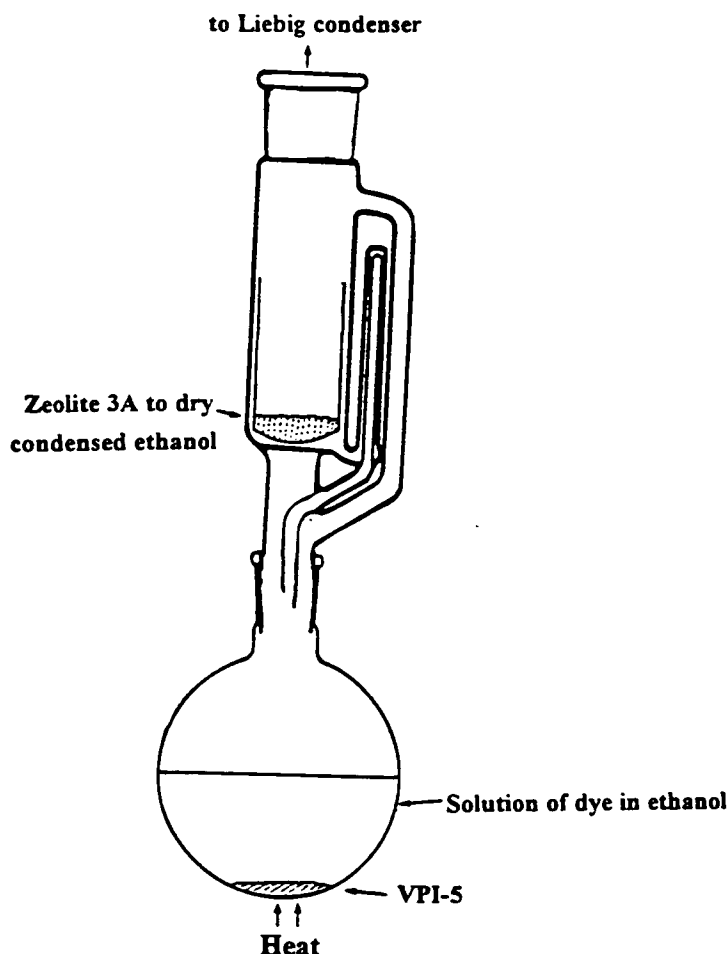
Evaporation of solvent. Acetone and methylene chloride were used, both with as-made VPI-5 and VPI-5 which had been boiled in the appropriate solvent. Again there was no success in forcing dye into VPI-5, samples took on little if any colour, and usually when evaporation of the solvent was complete there were discreet layers of VPI-5 and dye.

In the light of the results gained from work described in this section some further attempts were made to use solvents to aid the incorporation of dyes into VPI-5. The new methods involved the incorporation of apparatus designed to help remove water whilst solutions of dye were being heated with VPI-5. Two types of apparatus were used; a soxhlet extractor and a Dean and Stark trap

5.4.2 Use of a soxhlet extractor

Experimental. A soxhlet extractor was attached above a flask containing VPI-5 and a solution of dye in dry ethanol. The set-up is shown in Figure 5.10. Once the solution was boiling steadily and some ethanol had condensed in the soxhlet, the thimble was filled with freshly dried zeolite 3A. It was hoped that the 3A would dry condensed ethanol prior to its return to the flask and that this in turn would aid ethanol uptake into VPI-5. Thus, in a reversal of its usual role, the soxhlet extractor was being used to enable a substance to be extracted from the solvent below.

Figure 5.10
Use of a soxhlet extractor to assist sorption of dye into VPI-5



The solution was heated at reflux temperature for 5 hours, after which the VPI-5 was immediately filtered off and dried in a desiccator. Dyes used were waxoline yellow 3GPFW and dispersol yellow C-5GN.

The samples underwent similar investigation to those in section 5.4.1, they were also examined by Raman spectroscopy, as described in chapter 2.

Results. The mildly dehydrating conditions which this technique produced did seem to cause small amounts of the two dyes to be sorbed into VPI-5. However the quantities were very small: The filtered solids were an even pale yellow in both cases, the dyes were easily washed out and the VPI-5 structure was not thermally stabilised. Despite this, evidence that the dyes were sorbed came from Raman spectroscopy. Spectra showed a very slight broadening of the dye peaks compared to those seen in the spectra of pure dyes.

In order to determine whether the broadening of Raman peaks really was due to interactions between sorbed dyes and the VPI-5 framework, spectra of the following samples were also collected:

- Dye ground with VPI-5 and heated at 95°C overnight, then washed with ethanol until no more dye could be removed.
- Dye ground with $\text{AlPO}_4\text{-8}$ and heated at 95°C overnight.
- Dye heated at 95°C overnight.
- Dye slurried with ethanol and allowed to dry.
- A solution of dye in ethanol.

Both of the dyes were investigated and for both of them only the first of the above samples showed any broadening of the dye peaks. From the results given in 5.5.1 it was known that in such samples any remaining dye was trapped inside an $\text{AlPO}_4\text{-8}$ framework, as heating would have caused some dye to enter the pores but would also have caused the VPI-5 structure to collapse, thereby trapping the sorbed dye. Washing then removed all external dye.

Thus, from the absence of peak broadening in the other samples, external sorption onto aluminophosphate or the presence of ethanol could be ruled out as causes of the peak broadening in the original samples of dye sorbed into VPI-5 from ethanol. It had also been shown that broadening was not due to the effects of temperature upon the dye in the heated sample. Therefore these results showed that:

i) Sorbed dyes interacted with the aluminophosphate framework such that the peaks of their Raman spectra were broadened.

ii) Dye was sorbed into VPI-5 from ethanol solution when water was actively removed from the system.

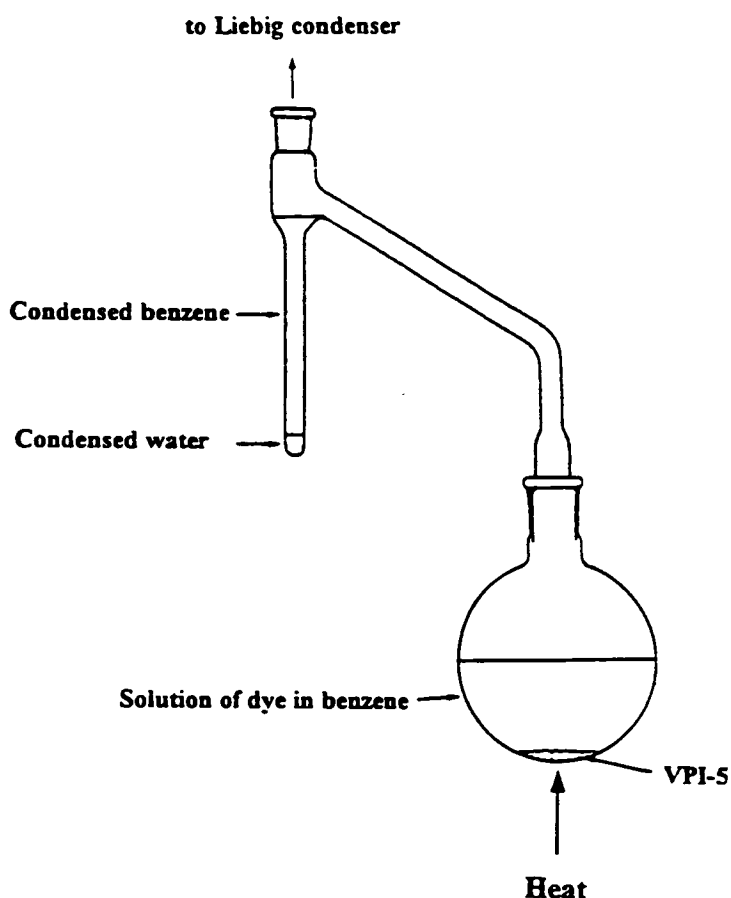
Unfortunately the loadings produced by this technique were small as were the Raman effects caused by interactions. The technique was therefore deemed unlikely to produce any interesting effects.

In conclusion, dehydration by soxhlet was able to cause dye to be sorbed into VPI-5 from solvent, however the amounts sorbed were very small so that the samples were barely coloured. There was no stabilisation of the VPI-5 framework, and interactions between dyes and framework were small. On the positive side sorption itself had been achieved without $\text{AlPO}_4\text{-8}$ formation. This suggested that more appropriate solvents or dyes, or the use of more dehydrating conditions might enable good loadings of dye into VPI-5 to be achieved from solvent.

5.4.3 Dean and Stark Trap.

Experimental. The Dean and Stark trap was set up as shown in Figure 5.11. The idea of the trap is that it enables two immiscible liquids to be separated, with the denser one staying in the bottom of the trap, whilst the less dense one can flow back into the flask.

Figure 5.11
Dehydration of VPI-5 by benzene, using a Dean and Stark trap



None of the previously used solvents were suitable for the task of removing water by this method and so another had to be found. Benzene was a possibility since it is used to dry ethanol through the formation of an azeotrope with water. However in view of the toxicity of benzene an alternative was sought. It was thought that toluene might be of use. With its boiling point being higher than that of water it was thought that a boiling solution of toluene should be able to force water to leave VPI-5.

Prior to the use of dye, the stability of VPI-5 in boiling toluene was checked. A small amount of VPI-5 was heated in toluene for 5 hours, with a Dean and Stark trap attached. By the end of that time water could definitely be seen at the bottom of the trap. Unfortunately XRPD analysis of the dried product showed that there had been $\text{AlPO}_4\cdot 8$ formation. The temperature of boiling toluene (110°C) had been too high for VPI-5 and so benzene (b.p. = 80°C) was used instead.

When VPI-5 was heated in boiling benzene, water could again be seen in the bottom of the trap after 5 hours. This time XRPD analysis showed the VPI-5 to have remained intact. The process was therefore repeated using solutions of dye in benzene.

The only dye for which this technique was explored was waxoline blue APFW, since work was at that time concentrating solely on getting that dye into VPI-5. Conditions used were as follows: VPI-5 (0.5g) was heated in 0.05M waxoline blue APFW in benzene (125ml) for 3, 12 and 30 hours. Solids were recovered by filtration and washed with a small amount of benzene.

Samples were analysed similarly to those from Section 5.4.1. There was also much investigation of the thermal stability of the samples of VPI-5 loaded with waxoline blue APFW from benzene. The dye was expected to improve the thermal stability of VPI-5, however it was thought that sorbed benzene might have an adverse effect. Because of this some of the samples prepared via the Dean and Stark trap were further treated by boiling in water in an attempt to drive out benzene.

Results. Heating VPI-5 in toluene for five hours with a Dean and Stark trap attached led to approximately 80% conversion to $\text{AlPO}_4\cdot 8$. With benzene as solvent the trap proved to be very effective at partially dehydrating VPI-5 without causing $\text{AlPO}_4\cdot 8$ formation. The amount of water removed from the trap after the initial stability test, in which 1g VPI-5 as heated in 80ml benzene, was approximately 0.1ml. This was equivalent to about 40% of the initial water content of the VPI-5 and so represented a sizable dehydration.

When solutions of waxoline blue APFW were used the filtered VPI-5 was very strongly coloured. Simple washing was not very effective at removing the colour but most could be removed by soxhlet extraction with methylene chloride.

Thermal analysis showed that total weight loss from the VPI-5 remained at about 25%, but that only 19% was water in the sample heated for 3 hours and only about 16% in the samples which were in benzene for 12 and 30 hours. The remainder was attributed to dye and benzene.

The thermal analysis traces are shown in Figure 5.12 and they can be seen to be very similar for the samples which were in benzene for 12 and 30 hours. This suggested that an upper limit of dye uptake might have been reached. Interestingly however the amount of water which remained in the 12 and 30 hr samples was approximately the same as that which had remained in the test sample of VPI-5 heated in benzene. This suggested that there might be a limit to the amount of water which benzene could remove from VPI-5.

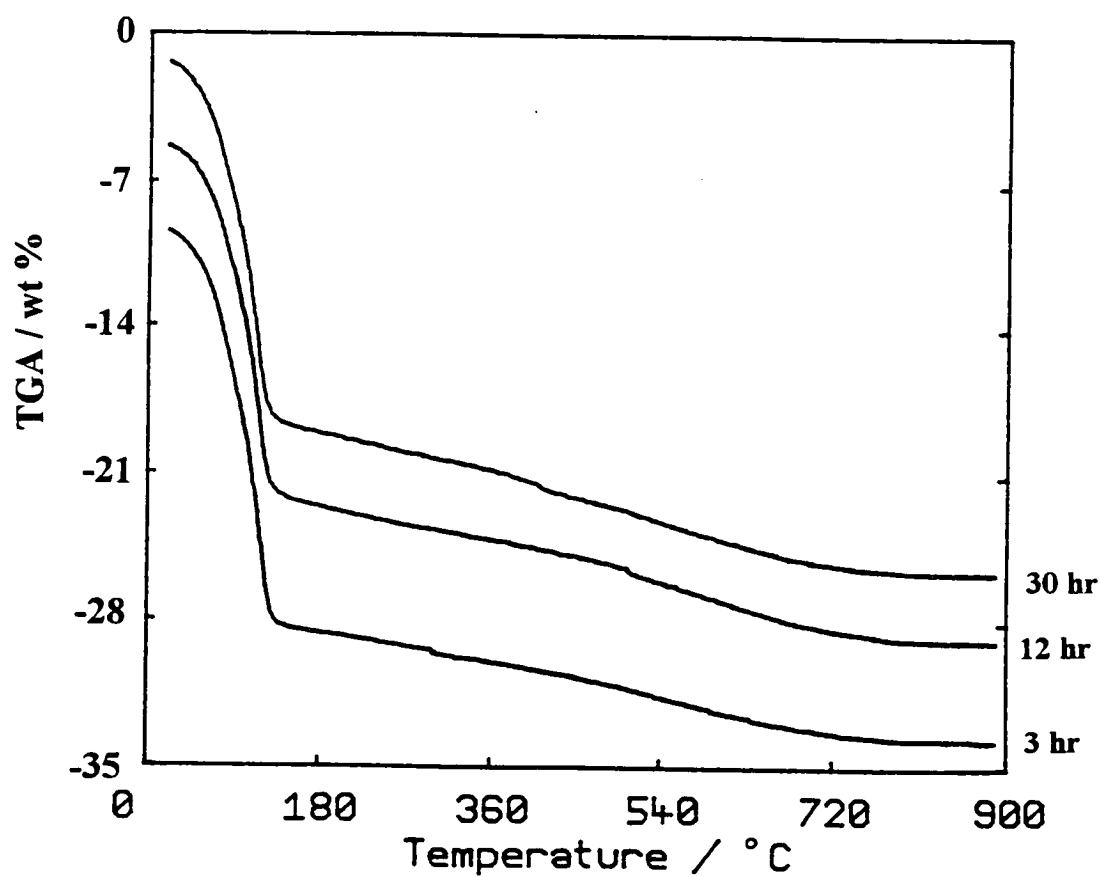
A study of the thermal stability of the VPI-5 in the three samples heated at 80°C in open vials was carried out. Table 5.4 lists the amounts of $\text{AlPO}_4\cdot 8$ formed when samples were heated.

Table 5.4 The thermal stability of samples of VPI-5 loaded with Waxoline Blue APFW from benzene solution.

Time heated at 80°C →	4 hr	8 hr	16 hr
Time in solution ↓	% $\text{AlPO}_4\cdot 8$		
3 hr	75	83	80
12 hr	63	62	67
30 hr	62	66	69

These figures show a small but definite increase in thermal stability between the three hour sample and the others. They also show that the VPI-5 in those other two samples has very similar thermal stability. This therefore supports the view that for whatever reason there was no more dye in the 30 hr sample than in the 12 hr sample.

Figure 5.12 Thermal analysis traces of VPI-5 heated with solutions of waxoline blue in benzene



Length of time in hot dye solution	Total weight loss	Weight loss below 180°C - attributed mainly to water	Weight loss above 180°C - attributed to benzene and dye
3 hr	24.2 %	20.5 %	3.7 %
12 hr	23.6 %	17.3 %	6.4 %
30 hr	24.3 %	17.7 %	6.6 %

Since VPI-5 contacted with hot benzene alone showed no gain in thermal stability, the increases could only be attributed to dye sorbed into VPI-5 from the benzene solutions. Efforts to increase VPI-5 thermal stability by boiling the samples in water in fact led to poorer stability. This unexpected result was thought to be due to the fact that dye and benzene were associated and so desorbed together when benzene was forced out by water. It was not thought likely that water had displaced the dye alone because samples of VPI-5 and waxoline blue APFW in other experiments had been boiled in water without any loss of stability.

In conclusion this method of loading VPI-5 with dye proved to be able to put small amounts of dye in. With waxoline blue APFW a limit was reached on the quantity sorbed which was too low to have a large effect on the thermal stability of VPI-5. Water proved to be able to desorb much of the dye, possibly because of an interaction between dye and benzene. A positive advantage of this method was that, unlike the heating of physical mixtures, there was not a large quantity of dye left outside the crystals after loading.

5.4.4 Attempts to load VPI-5 with C₆₀

It is appropriate at this point to briefly diverge away from work with dyes. At around the same time as Dean and Stark traps were being used with benzene solutions, there appeared a paper by Anderson *et al* [10] in which the confinement of buckminsterfullerene in VPI-5 was described. They impregnated C₆₀ into VPI-5 from a solution in benzene and reported that the composite exhibited enhanced VPI-5 stability and also interesting optical properties. An attempt was made to repeat their work, since the properties described for the composite appeared to fit the description of what was looked for in the project.

Experimental. Dr M. Banks (Edinburgh University) supplied 92mg of C₆₀ which had been purified by chromatographic separation. This was dissolved in AnalaR benzene (100ml) which had been further purified by partial distillation. After ultrasonification for several hours, to aid dissolution, the solution was filtered through a glass sinter.

Washed VPI-5 (0.25g) was heated in the purple solution, in a 250 ml round-bottomed flask with a Dean and Stark trap attached, in the same way as in 5.4.3. The system was heated for 30 hours.

This procedure for recovery of VPI-5 from the flask was complicated by the need to minimise C_{60} losses. In order to recover the VPI-5 the contents of the 250 ml round-bottomed flask were transferred to a conical flask and water was slowly and carefully added, to give two layers. The flask was left to stand overnight, the benzene layer was decanted off and VPI-5 was recovered from the remaining aqueous layer by filtration.

At Edinburgh the crystals were analysed by XRPD and thermal analysis, as well as having their thermal stability investigated. They were sent, through Dr P. Langridge-Smith (Edinburgh University), to Dr K. O'Donnell at Strathclyde University to have their optical properties investigated.

Results. The recovered VPI-5 was dark brown which indicated that there had been uptake of C_{60} . Further evidence that C_{60} was successfully sorbed into VPI-5 came from thermal analysis of the prepared sample and also from XRPD analysis of portions of the sample which were heated in air.

Figure 5.13 shows the thermal analysis trace in which it can be seen that there is a weight loss at high temperatures. The loss is approximately 2% w/w and, although some of the loss may have been due to trapped benzene, the majority was attributed to sorbed C_{60} . The XRPD pattern shown in Figure 5.14 shows that part of the VPI-5 structure remained intact after the complex was heated to 950°C , which indicated that there had been partial stabilisation of the framework. There was however 76% conversion to $\text{AlPO}_4\text{-8}$, suggesting that C_{60} did not have a large positive effect upon the thermal stability of VPI-5 thermal stability, despite the relatively large amount which was sorbed. The most likely reason for that is that C_{60} is too small (diameter 6.8 Å) to act as a good structural scaffold for the 12 Å channels of VPI-5.

Despite success in the sorption of C_{60} into VPI-5, the workers at Strathclyde University failed to find any novel optical properties of the complex.

Figure 5.13 The thermal analysis trace of a VPI-5/C₆₀ complex

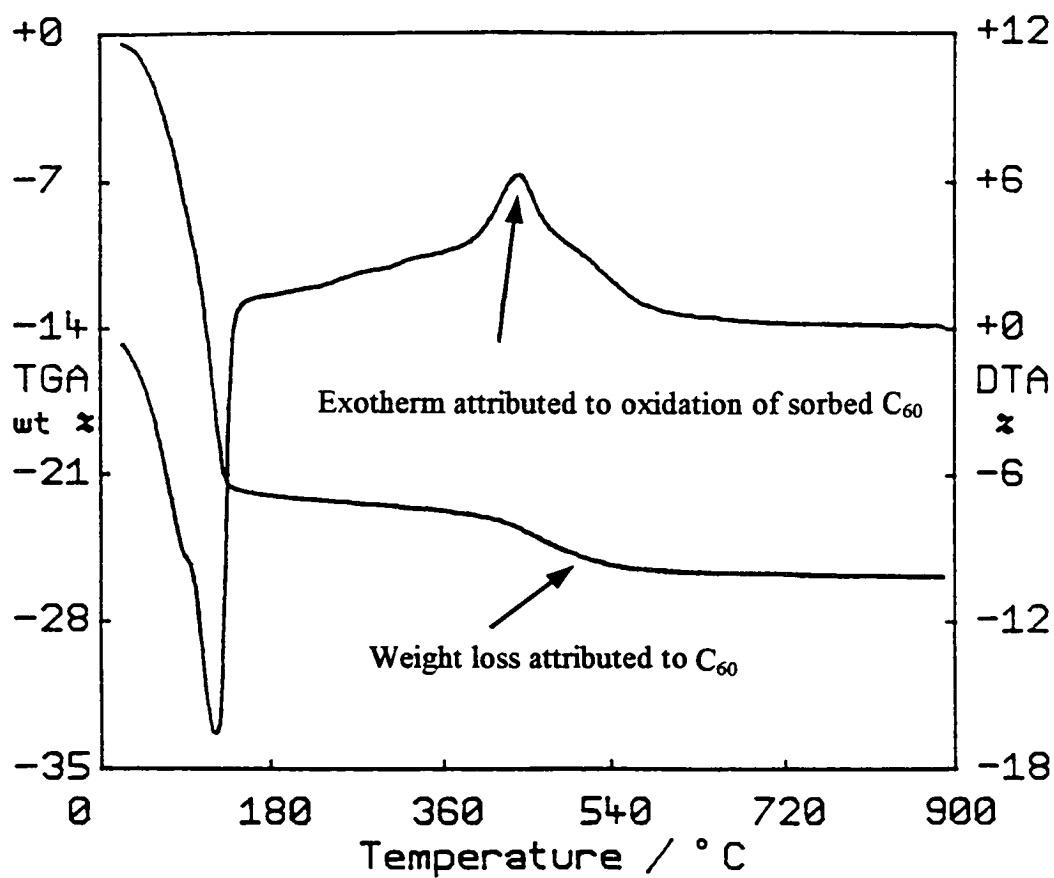
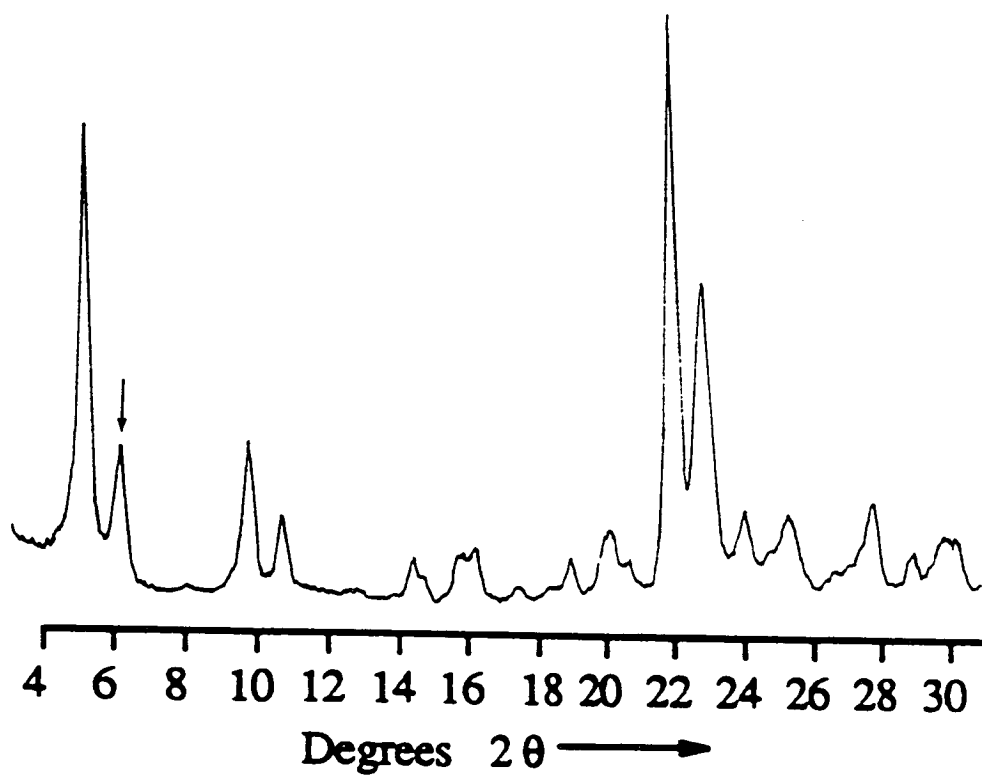


Figure 5.14 The XRPD pattern of a heated VPI-5/ C_{60} complex



An $AlPO_4-8$ content of 76% indicates slight stabilisation of VPI-5, which indicates uptake of C_{60} .

5.5 Use of FEP Tubing.

The investigations detailed in sections 5.2 - 5.4 had covered a wide range of methods by which dye might be loaded into VPI-5. The best results had come from the use of capped vials which allowed a slow release of water when heated, however as has been said, that route was not consistently reproducible and so another route was looked for which would operate in a similar, but more controllable manner.

The solution which was hit upon came from the work of K.C.Franklin [11]. He had been looking for cheap unreactive reaction vessels in which to carry out synthesis studies on aluminophosphate molecular sieves and had come across fluoroethylene polymer [FEP] tubing. Like PTFE this material is very unreactive, but it has the advantages of being easy to seal, as described in chapter 2, and of being cheap enough to throw away after a single use. Unfortunately for Dr Franklin it soon turned out that the disadvantage (to him) of FEP was that it became permeable to water when heated, thus all of his reactions dried out.

It was however a positive advantage to this work that the material should become permeable to water when heated, especially coupled with its ability to be easily sealed. The idea was that by use of standard lengths of tubing and standard weights of VPI-5 it would be possible to find an optimum temperature at which the FEP released water very slowly and at which dye was mobile enough to fill the VPI-5 pores as they were dehydrated. The diameter of the tubing which was used was $\frac{1}{4}$ " internal, $\frac{5}{16}$ " external.

5.5.1 Initial work.

Experimental. A sample size of 100mg of mixture at 10% w/w dye was chosen, to be put into 9cm FEP tubes. Temperatures of 80°C and 95°C were used initially and waxoline blue APFW was the dye used. Tubes and samples were very carefully weighed so that estimates of the rates of water loss might be calculated afterwards. The tubes were heated for 7 days and reweighed as soon as they were taken from the ovens. This showed neither sample to have been totally dehydrated and so they were placed back in the oven for a further 5 days. Upon removal from the ovens for a second time, the tubes were allowed to cool to room temperature before they were cut open and the contents recovered.

Results. The rates of water loss calculated from the weights of the tubes after 7 days of heating were:

$$95^{\circ}\text{C} \dots\dots 7.5 \times 10^{-6} \text{ g cm}^{-1} \text{ hr}^{-1}$$

$$80^{\circ}\text{C} \dots\dots 4.1 \times 10^{-6} \text{ g cm}^{-1} \text{ hr}^{-1}$$

95°C. The sample heated at 95°C contained $\text{AlPO}_4\text{-8}$, the amount of conversion being about 40%. Thermal analysis suggested that a small amount of dye was in the channels, however it was a very small amount and not enough to prevent further conversion to $\text{AlPO}_4\text{-8}$. This was seen when XRPD analysis of the thermal analysis residue showed that approximately 90% of the framework was now $\text{AlPO}_4\text{-8}$. Thus 95°C had been too high a temperature. No further work was done with this sample.

80°C. The sample which was heated at 80°C still contained 100% intact VPI-5. Thermal analysis indicated that about 1% w/w of dye was sorbed into the channels. Table 5.5 lists the amounts of $\text{AlPO}_4\text{-8}$ formed when the 80°C sample was heated in air at various temperatures and Figure 5.15 shows some of the XRPD patterns of the products.

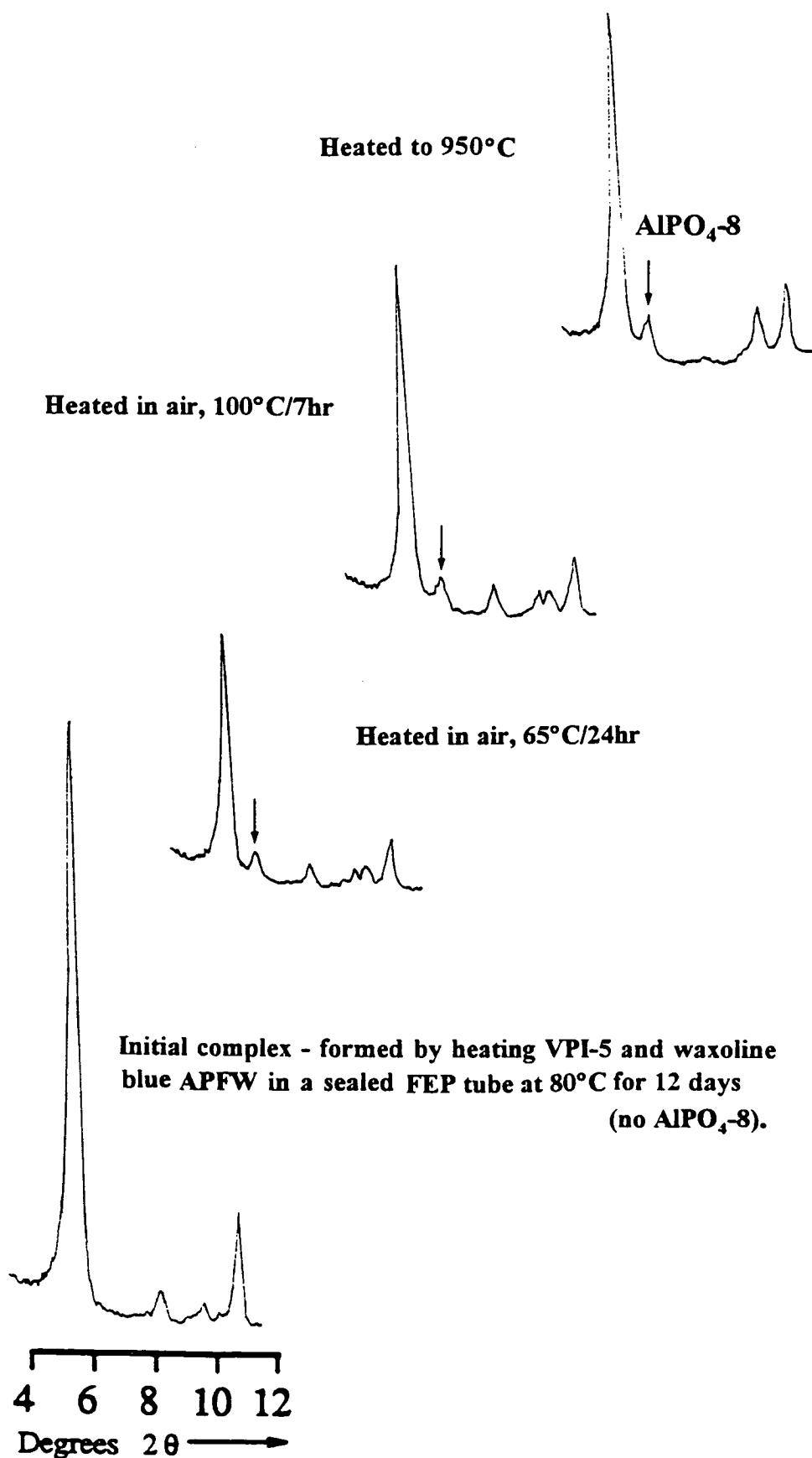
Table 5.5 The amount of $\text{AlPO}_4\text{-8}$ formed when a sample of VPI-5 and waxoline blue APFW, previously heated at 80°C for 12 days in a sealed FEP tube, was heated in air.

Temperature (°C)	Heating time (h)	% $\text{AlPO}_4\text{-8}$ formed
65	24	49
65	48	51
100	7	47
950	See Chap. 2	51

It can be seen that the thermal stability of the VPI-5 in the sample was enhanced but not greatly, which fits with a loading of 1%. A small amount of the sample was Soxhlet extracted with ethanol for 6 hours. This removed all but a trace of dye and all VPI-5 thermal stability was lost.

Thus, if VPI-5 was to be fully stabilised by complexation with dye, 95°C was too high a temperature at which to heat the mixture whilst 80°C was too low unless very long heating times were to be contemplated.

Figure 5.15 XRPD patterns of a VPI-5/waxoline blue APFW complex heated in air



5.5.2 Screening of dyes.

In order to further narrow down the number of dyes to be studied, the seven dyes listed below were screened in order to see which were the most promising in their ability to be sorbed into and to stabilise VPI-5.

Waxoline orange EPFW

Waxoline orange 3GPFW

Waxoline yellow 2GPFW

Waxoline yellow 3GPFW

Waxoline red O

Dispersol yellow C-5GN

H113471

Experimental. Mixtures were made by grinding with VPI-5 (10% w/w dye), with the idea that those which gave the best results would be used in further work.. The mixtures were treated in the same way as the best waxoline blue sample, *i.e.* 100mg into a 9cm FEP tube which was sealed and heated at 80°C for 12 days. At the same ^{time} a blank which contained only VPI-5 was heated.

Although the work of section 5.5.1 had shown that 80°C was probably too low a temperature at which to heat waxoline blue APFW with VPI-5 in FEP tubes, and therefore presumably too low for the other dyes also, no other oven was available at the time which was why work was done at 80°C.

The recovered contents from the heated tubes were analysed by XRPD for signs of $\text{AlPO}_4\cdot 8$ formation. They were also examined visually for any colour change which might indicate interaction of dye with VPI-5. In order to test for thermal stability, portions of the heated samples were heated again at 80°C, but this time in open tubes so that water could readily escape. The samples were heated for 24 hours, cooled and examined by XRPD.

Further clues on whether or not the dye had been sorbed were given by thermal analysis, which, by XRPD examination of the residues, also gave information on the thermal stability of their VPI-5 when heated to 950°C.

Results. Analysis of the heated products by XRPD showed that none contained any $\text{AlPO}_4\text{-8}$ after their 12 days of heating in an FEP tube. Visually however the colours were little different from those of the physical mixtures, which suggested that there had been little uptake of dye for, as was seen earlier (5.2), dye uptake was expected to have been accompanied by colour change in most cases.

Thermal analysis traces for most of the heated samples were very similar to the traces of the corresponding physical mixture. Therefore this too suggested that little or no dye had been sorbed into the VPI-5. The only exceptions were waxoline orange EPFW and waxoline orange 3GPFW where differences between the TGAs and DTAs of the physical mixtures and heated mixtures suggested that there may have been some dye sorption.

In terms of thermal stability the results were generally as expected. The amount of $\text{AlPO}_4\text{-8}$ formation was mainly greater than for waxoline blue APFW, between 65 and 75%, so not too good, although better than had been obtained when mixtures had been heated in open tubes.

There were two exceptions of thermal stability which did not give 65-75% $\text{AlPO}_4\text{-8}$ when heated:

The first was waxoline orange 3GPFW, one of the dyes which thermal analysis indicated might be slightly sorbed into VPI-5. For the sample which contained this dye, the amount of $\text{AlPO}_4\text{-8}$ formed upon heating was only 50%, comparable therefore with waxoline blue APFW.

The other exception was pure VPI-5, which was intact when removed from the FEP but which completely collapsed to 100% $\text{AlPO}_4\text{-8}$ when heated in air. This was expected but served to prove that increased stability was due to the presence of dye and not an effect of the VPI-5 being heated.

The idea of this experiment had been to screen the dyes in order to find two or three others on which to concentrate alongside waxoline blue APFW. It had been shown conclusively that the sorption of dyes influenced the thermal stability of VPI-5, they appeared to act as structural scaffolds, inhibiting the transformation to $\text{AlPO}_4\text{-8}$. Each dye enhanced the stability a different amount and the more dye that was sorbed the better the effect in general. Therefore it was not just effects on the sorbed dyes that were looked for, a lot of study was done on the thermal stability of dye-loaded VPI-5,

for dyes that could prevent $\text{AlPO}_4\text{-8}$ formation were going to be able to keep the pores open and so achieve high loadings. Note though that stability of VPI-5 indicated sorption of dye, but lack of stability did not necessarily indicate lack of sorption since the effect was thought to be strongly size-related and so small dyes may not have been able to prevent $\text{AlPO}_4\text{-8}$ formation. With these points in mind the three dyes which were chosen were:

- Waxoline orange 3GPFW - an obvious choice since it had shown signs of sorption into VPI-5 at 80°C and had had a large effect upon the thermal stability of VPI-5.
- Waxoline orange EPFW - though it had not had a notable effect upon the thermal stability of VPI-5 there had been indications that some of this dye was sorbed at 80°C and so it was chosen on the grounds that optimised heating conditions might lead to high loadings.
- H113471 - the next best increase in thermal stability of VPI-5 was produced in the sample which contained this dye, so although thermal analysis did not indicate significant sorption it was thought that there must have been some and so this dye was chosen for its ability to stabilise VPI-5.

5.5.3 New temperatures.

Experimental. As was seen 80°C was not an ideal temperature at which to heat dye mixtures in FEP tubes. It seemed that the rate of water loss was far too low. Therefore, when ovens became available, some more dye / VPI-5 mixtures were heated in FEP tubes at new temperatures. An initial screening looked at the use of waxoline blue APFW at 85, 90, and 93°C days. Further work investigated the use of the other 3 dyes, chosen from 5.5.2, at temperatures of 90 and 93°C for seven days, as well as heating samples of VPI-5 with waxoline blue APFW at 90°C for 30 days and 93°C for 40 days.

All products from the FEP tubes were analysed, as before, by XRPD and thermal analysis. The thermal stabilities of those which emerged intact from the FEP tubing were investigated.

These experiments covered two options for trying to get higher dye loadings; longer heating times at the same temperature or similar heating times at higher temperatures, though mainly the second one of higher temperatures. The earlier work had shown 95°C to be too high a temperature hence why 93°C was the highest temperature used.

Results.

Waxoline Blue APFW. All of the initial mixtures of VPI-5 with waxoline blue APFW, heated in FEP tubes for seven days at 85°C, 90°C or 93°C contained intact VPI-5 upon removal from the FEP. The thermal stabilities of the samples were investigated and table 5.6 shows the results of when they were heated in air.

Table 5.6 The amount of $\text{AlPO}_4\text{-8}$ formed when samples of VPI-5 and waxoline blue APFW, previously heated in sealed FEP tubes, were heated in air.

Temperature at which sealed FEP tube was heated	Temperature and time of heating in air	
	80°C/12h	950°C
80°C / 7d	50%	51%
85°C / 7d	20%	74%
90°C / 7d	13%	34%
93°C / 7d	30%	35%

Despite apparent scatter, the results in the table show that thermal stability appeared to have increased over that of the sample which had been heated in FEP at 80°C, certainly for the 90 and 93°C samples.

The improved stabilities were attributed to higher loadings of dye, however the TGA traces of the samples were little different from that of the 80°C sample. In all cases the method of determining the amount of sorbed dye indicated that the samples had the same amount of dye: just under 1% w/w, dye / VPI-5.

The method of determination was to compare the TGA trace of the heated sample with that of a physical mixture of VPI-5 and waxoline blue APFW. Any extra weight loss at high temperatures was attributed to the calcination of sorbed dye.

It seemed that there was a fault with the method, for not only did the different thermal stabilities indicate different amounts of dye uptake but the stabilities which were seen with these samples were as high or higher than were encountered in the samples heated in capped vial (5.3.3). In that sample the edges of the crystals had transformed to $\text{AlPO}_4\text{-8}$ which had trapped all of the sorbed dye. Thermal analysis had then shown that the complex contained 4% w/w waxoline blue APFW.

In contrast there was no $\text{AlPO}_4\text{-8}$ formation, and hence pore blockage, when the samples were heated in the FEP tubes. It is believed this enabled much sorbed dye to desorb during thermal analysis, with only small amounts being trapped such that they calcined out at high temperatures. Therefore TGA indicated much lower levels of dye sorbed into the framework than actually occurred. The outcome of this discovery was that thermal analysis traces could not, in many cases, be relied on to give good quantitative results of the amount of dye which had been sorbed into the pores of VPI-5.

Longer times. The samples of VPI-5 and waxoline blue APFW which were heated at 90°C for 30 days and 93°C for 40 days did not emerge from the tubes intact. The amounts of $\text{AlPO}_4\text{-8}$ formed were:

90°C for 30 days 56%.

93°C for 40 days 70%

The results seemed to be peculiar for extended heating at 90°C or 93°C caused large amounts of supposedly stable VPI-5 to convert to $\text{AlPO}_4\text{-8}$.

There may however be an understandable reason for the large amounts of $\text{AlPO}_4\text{-8}$ which formed upon extended heating. The suggested reason is that as dye moved around the hot VPI-5, small areas devoid of dye may have formed temporarily. This is probable because there would essentially be a one-dimensional string of dye within the channels rather than a bulk three-dimensional system. If a void formed there would be the possibility that that part of the VPI-5 framework could convert to $\text{AlPO}_4\text{-8}$, especially at 80°C where there would still be water vapour present. This would of course be an irreversible change, so extended heating would lead to more and more $\text{AlPO}_4\text{-8}$ formation.

If this explanation is correct then the implication would be that the use of dyes to stabilise VPI-5 could only be considered for relatively short periods, though since these could still be of the order of days it might not be too serious. Possibly more serious was the fact that it meant that it made this method of dye sorption less attractive, no longer could it be considered as a gentle way whereby dyes could be given virtually as long as they needed to fill up the channels of VPI-5.

Other Dyes. The next batch of FEP experiments had involved heating mixtures of VPI-5 and waxoline orange 3GPFW, waxoline orange EPFW, or H113471 at 90 or 93°C for seven days.

With the exception of VPI-5 and H113471 heated at 90°C, all of the samples were removed from their sealed FEP tubes with fully intact VPI-5. A pinhole caused by poor sealing was found to be the cause of the bad result. The affected sample was not investigated further, however the thermal stability of the VPI-5 in the other samples was looked at, Table 5.7 shows how much $\text{AlPO}_4\text{-8}$ formed when the samples were heated.

Table 5.7 The amounts of $\text{AlPO}_4\text{-8}$ formed when samples of VPI-5 which contained dye were heated in air.

Dye	Temperature at which sealed FEP tube was heated	Conditions of heating in air ^a	% conversion of VPI-5 to $\text{AlPO}_4\text{-8}$
Waxoline orange 3GPFW	90°C	80°C/24h	NIL
	90°C	950°C	19%
	93°C	80°C/24h	NIL
	93°C	950°C	NIL
	93°C	750°C	Trace
H113471	93°C	80°C/24h	Trace
	93°C	950°C	49%
Waxoline orange EPFW	90°C	80°C/24h	NIL
	90°C	950°C	NIL
	90°C	750°C	Trace
	93°C	80°C/24h	35%
	93°C	950°C	44%
	93°C	750°C	47%

^a See Chapter 2 for full details of the conditions used to heat samples to 750 and 950°C.

Figure 5.16 XRPD patterns of a VPI-5 / waxoline orange 3GPFW complex, showing greatly enhanced VPI-5 thermal stability

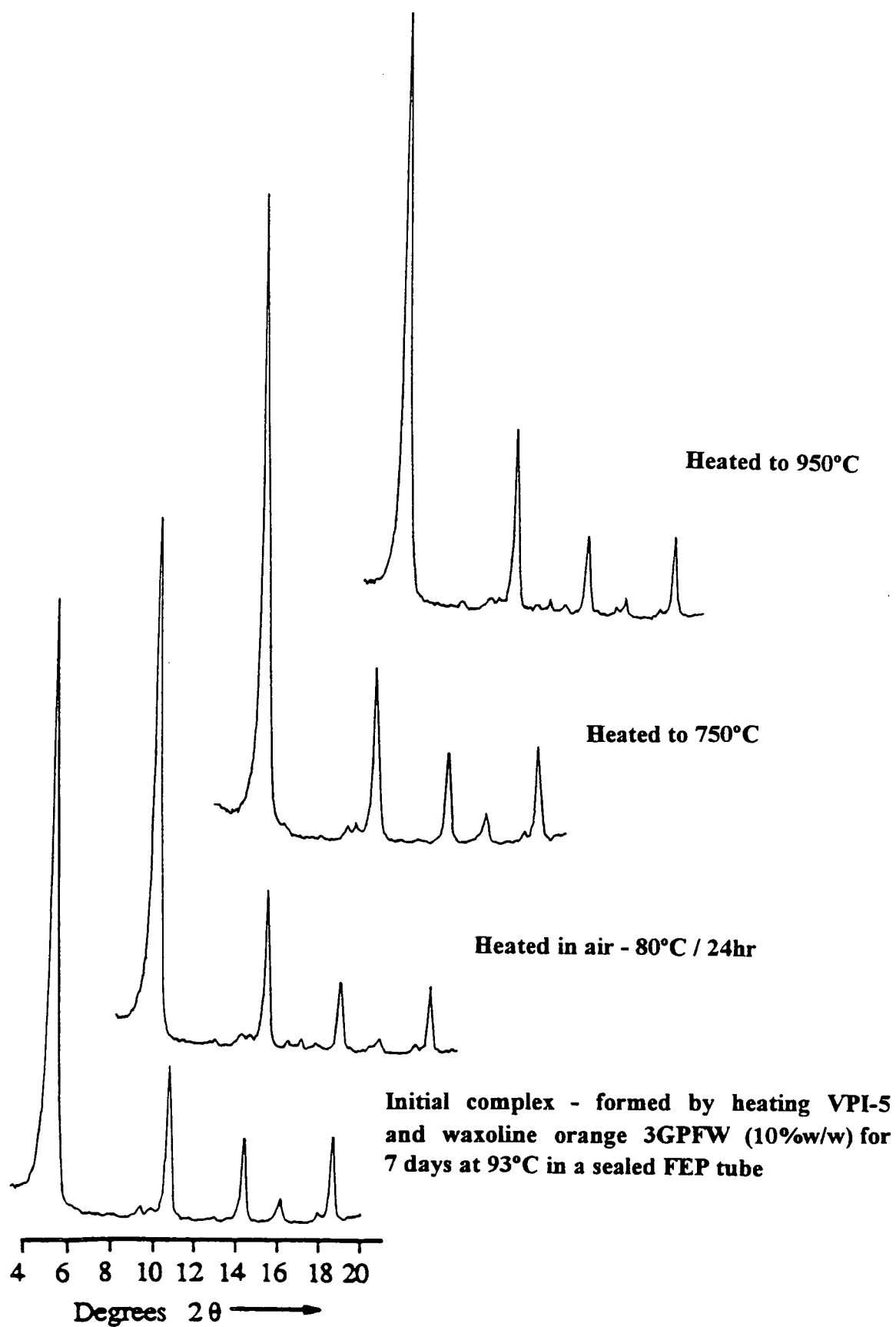
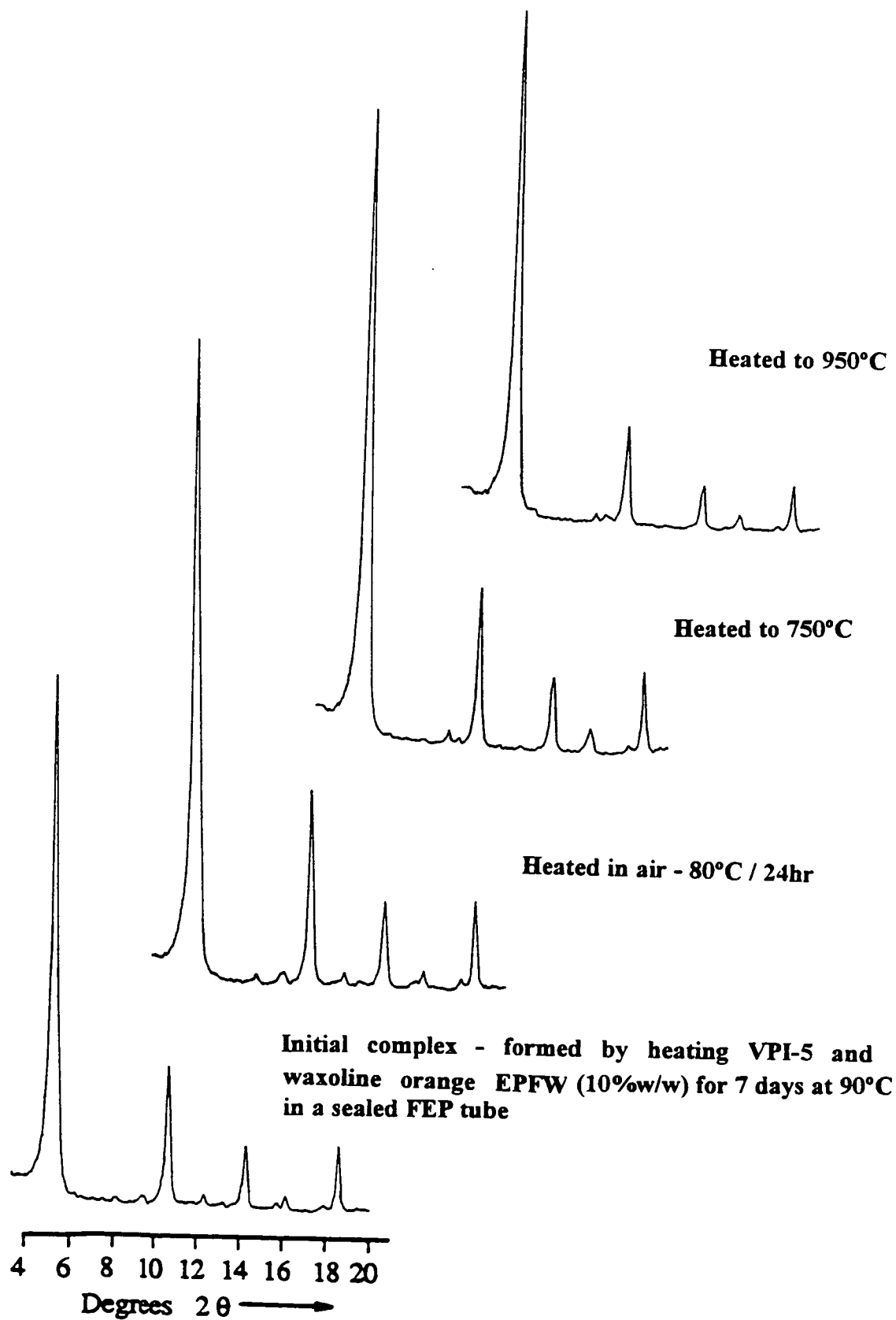


Figure 5.17 XRPD patterns of a VPI-5 / waxoline orange EPFW complex, showing greatly enhanced VPI-5 thermal stability

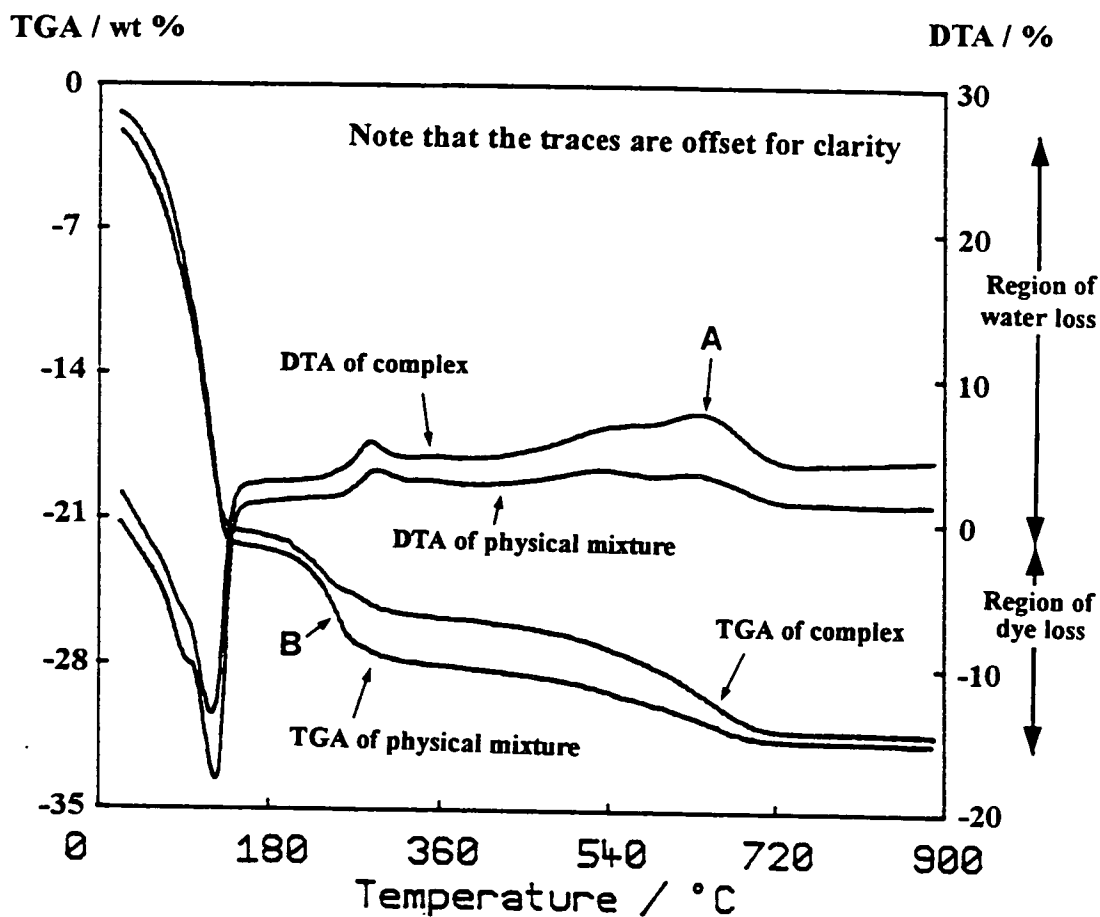


Here were some very interesting results: two dyes had managed to produce near complete stabilisation of VPI-5. Figures 5.16 and 5.17 show some of the XRPD patterns of the highly stabilised complexes, they show just how small the trace peaks of $\text{AlPO}_4\text{-8}$ were.

As with waxoline blue APFW, the thermal analysis trace of VPI-5 and waxoline orange 3GPFW did not give any clues as to the amount of sorbed dye, because it was very similar to the thermal analysis trace of an unheated physical mixture of VPI-5 and waxoline orange 3GPFW. The only difference was that there was a little less water in the stabilised sample.

On the other hand, as Figure 5.18 shows, there was a very obvious difference in the thermal analysis traces of VPI-5 and waxoline orange EPFW heated at 90°C and the corresponding physical mixture. The traces suggest that there was an uptake of waxoline orange EPFW equivalent to at least 2% of the weight of the sample. Since the sample contained about 10% dye and 20% water the amount of sorbed dye becomes nearly equivalent to 3% w/w with respect to dry VPI-5, a significant uptake.

Figure 5.18 A comparison of the thermal analysis traces of a heated complex and a physical mixture of VPI-5 and waxoline orange EPFW



A Large exotherm attributed to sorbed dye

B Dye lost at lower temperatures from the physical mixture than from the complex

5.5.4 Use of APHE-VPI-5.

Experimental. Only DPA-VPI-5 had been used in all of the work with dyes. This was because the quantities of APHE-VPI-5 which were available were too small. By the end of the project enough had been amassed, however, to have a number of attempts at loading dye into APHE-VPI-5 through heating mixtures in FEP tubing. Two tubes were made up, with waxoline orange 3GPFW as the dye, and these were heated at 93°C for 7 and 14 days after which they underwent the usual analysis. Two further tubes containing a similar mixture were heated for 9 and 11 days at 93°C.

Results. The batches of APHE-VPI-5 and waxoline orange 3GPFW which were heated in sealed FEP tubes for 7, 9 and 11 days all remained intact. That which was heated for 14 days did however contain a small amount of $\text{AlPO}_4\text{-8}$ and so was not further investigated.

The thermal stabilities of the samples heated for 9 and 11 days were poor; 24 hours at 80°C was enough for a substantial amount of their VPI-5 to convert to $\text{AlPO}_4\text{-8}$.

The star of the show was the sample which was heated for only 7 days. Portions were heated for 24 or 104 hours at 80°C, at 750°C, or analysed by thermal analysis (*i.e.* a programmed heating to 950°C in dry air). Through all of this the worst that happened, as shown in Figure 5.19, was the formation of a trace amount of $\text{AlPO}_4\text{-8}$ in a couple of the samples. The thermal analysis traces in Figure 5.20 show clear evidence of the sorption of dye; the amount being slightly more than 2% w/w with respect to dry VPI-5 framework, again a significant loading.

The results for APHE-VPI-5 at first seemed peculiar in that longer heating in FEP led to less stabilisation of VPI-5. In fact they would appear to support the theory that in a hot sample the mobility of the dye can lead to voids and so to a slow build-up of $\text{AlPO}_4\text{-8}$. There are then the corresponding pore blockages and hence lowered stability of VPI-5 as dye gets excluded from areas.

5.5.5 Conclusion

Heating physical mixtures of VPI-5 and dye in FEP tubing led to high levels of dye uptake. This in turn meant that the VPI-5 in many of the samples gained a high degree of thermal stability. Thus the benefits of controlled dehydration of VPI-5 had been shown.

Figure 5.19 XRPD patterns of an APHE-VPI-5 / waxoline orange 3GPFW complex, showing greatly enhanced VPI-5 thermal stability

* These peaks were due to surface dye

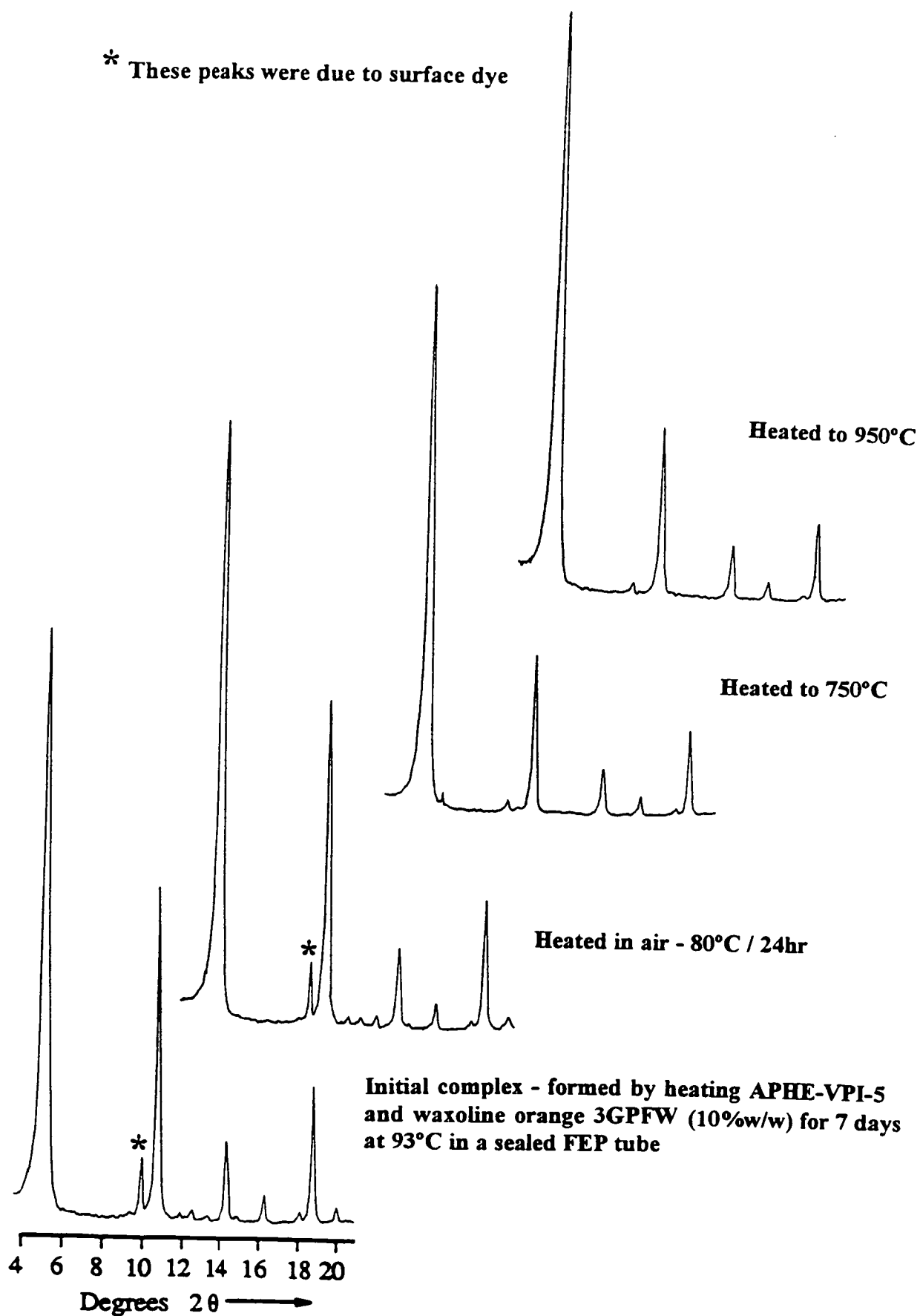
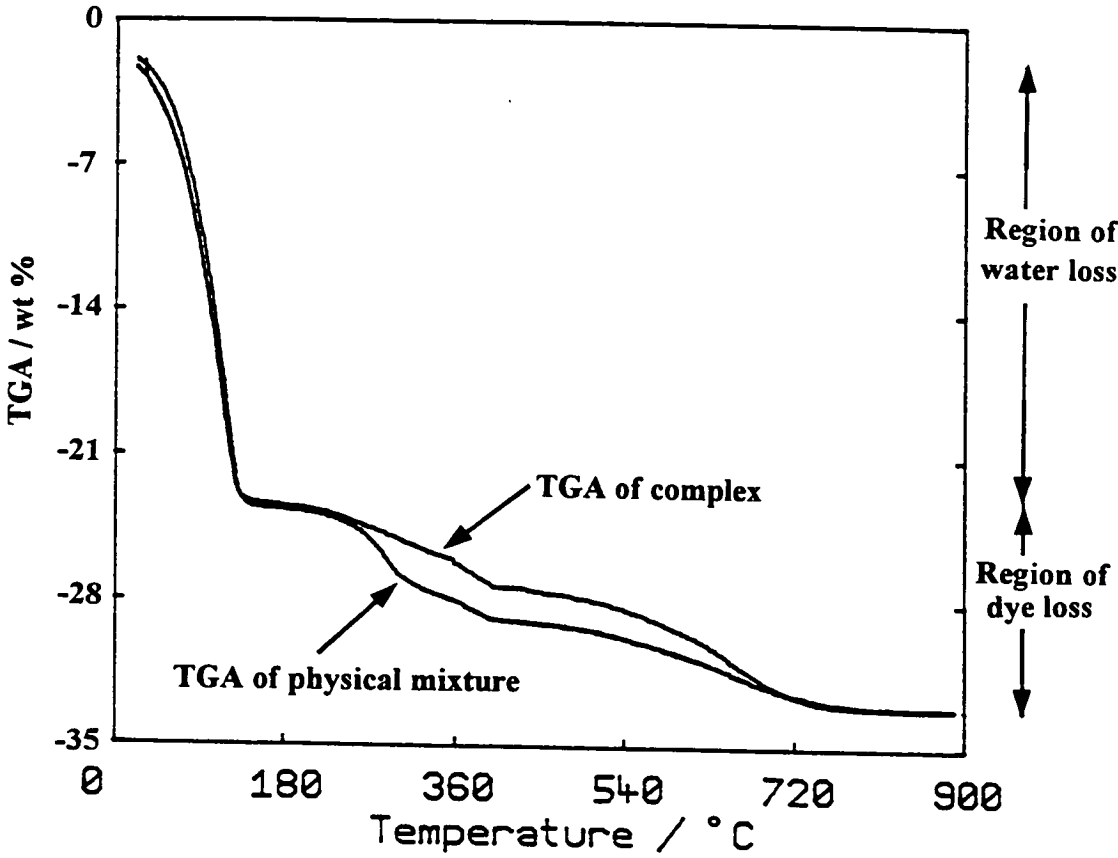


Figure 5.20 A comparison of the TGA traces of a heated complex and a physical mixture of VPI-5 and waxoline orange 3GPFW



Dye lost at lower temperatures from the physical mixture than from the complex

5.6 Photostability of Waxoline Blue APFW

As was mentioned at the start of the chapter, it was hoped to enhance the photostability of dyes by their sorption into molecular sieves. Through Dr W.N.E. Meredith (ICI Wilton) and Mr C. Bridle (ICI Wilton) an opportunity arose to test the photostability of a sorbed dye in the weathering facility at I.C.I. Wilton. In order to make the most of this opportunity the sample was chosen which contained the least photostable dye. This meant that any improvement should be obvious to see. The least photostable of the dyes under investigation was waxoline blue APFW. Helpfully it was also the most strongly coloured of the dyes which would further aid spotting any increase in photostability.

Experimental. Samples for weatherometer testing were prepared as follows;

i) Dye only - waxoline blue APFW (0.05g) was dissolved in ethanol (3.5ml). To this was added a solution of BT35 acrylic binder (20%) in water (1.0g) and NP8 surfactant (4 drops). The slurry was thoroughly mixed and a film drawn across 100µm Melinex plastic sheet with a Meyer bar (No. 4).

ii) Sorbed dye - waxoline blue APFW was thoroughly ground with VPI-5 (10% w/w dye). The mixture was heated at 95°C for seven hours, then at 80°C overnight. This caused some dye to be encapsulated within the framework of VPI-5/ AlPO_4 -8 which resulted. Some of the surface dye was removed by a light wash with ethanol. The dye/molecular sieve complex (0.5g) was slurried with a solution of BT35 acrylic binder (20%) in water (2.0g). A film was again drawn with a number 4 Meyer bar on the same substrate as the dye only samples.

iii) Acrylic binder - to give a control sample of resin only, a coating of BT35 was drawn on a sheet of 100µm Melinex O. This was done in case any yellowing of the resin might occur in the weatherometer, which might affect the look of the sample underneath. A number 2 Meyer bar had to be used as the resin coating cracked and peeled if a thicker coating was attempted.

Each of the three films was divided into several pieces, some of which were placed in the weatherometer and some of which were kept in the dark as controls. The weatherometer, a Xenotest 150S unit, subjected samples to intense UV irradiation in relatively dry conditions (65% relative humidity). Samples were removed after 310, 482, and 745 hours.

All samples were transferred to I.C.I. Runcorn and examined by visible spectroscopy, using a Perkin-Elmer Lambda-9 in transmission mode. Visual inspection of the samples was also carried out, with subjective estimations of colour loss made on the Grey scale.

Results. Figure 5.21 shows the UV/vis diffuse reflectance spectra of three samples prior to irradiation and after exposure to UV for 745 hours.

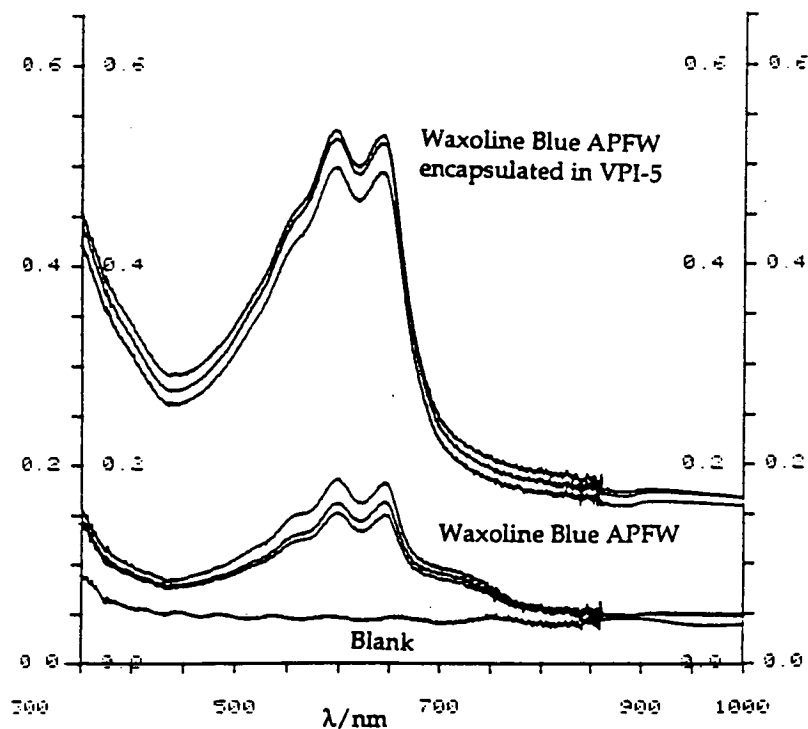
It can be seen that the sample which contained only dye was decolourised by UV: in fact visual examination determined that this occurred after less than 310 hours of irradiation.

The encapsulated dye still had colour after its irradiation. The spectra show, that there had been a shift in the absorbance to lower wavelengths. This was borne out by visual inspection which showed that the sample had become reddish. The result was still significant in making it clear that encapsulation altered the rate of loss of colour of waxoline blue APFW.

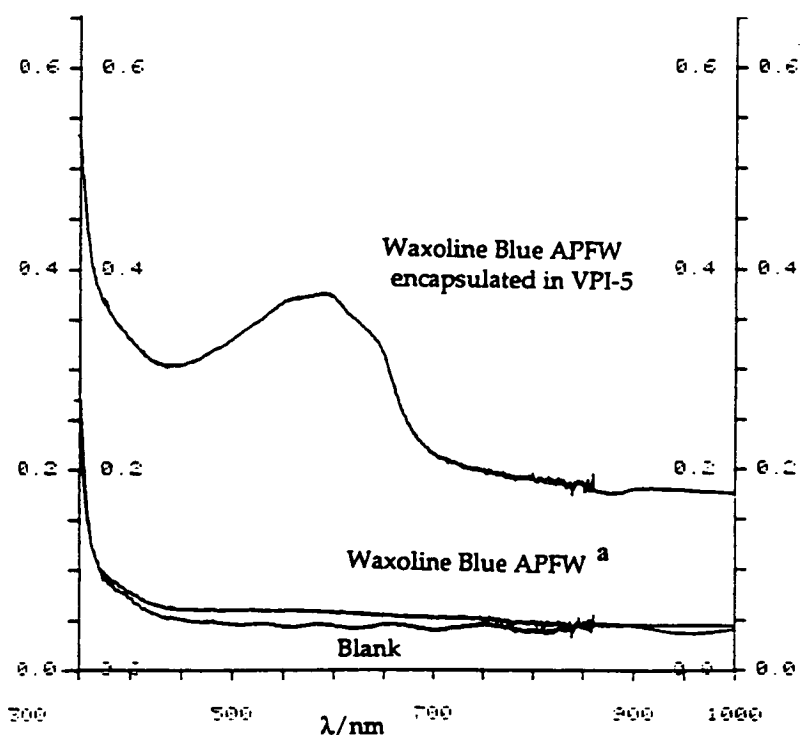
Conclusion. This experiment successfully showed that the encapsulation of waxoline blue APFW in VPI-5 led to some enhanced stability of the dye to irradiation. This very interesting phenomenon of enhanced photostability of trapped dyes would be a very worthwhile area for further study. Further, the blue to red fading which was observed was of interest because waxoline blue APFW is an anthraquinone derivative. Such materials are known to decompose by a dealkylation mechanism, through red intermediates [12]. These intermediates are, however, unstable and rarely observed, thus if they were being stabilised by the VPI-5 there would be another very interesting area of study.

Figure 5.21 Diffuse reflectance spectra of samples before and after UV irradiation

Diffuse reflectance spectra of samples prior to UV irradiation



Diffuse reflectance spectra of samples after exposure to UV irradiation for 745 hr



^a note this sample was removed from the weatherometer after 482 hours

5.7 Determination of Pore Volumes by Micromeritics.

One of the effects being looked for in this work was stabilisation of the VPI-5 framework. Therefore it seemed that measurement of micropore volumes might provide good evidence as to whether or not apparent stabilisation was being effective in keeping the pores of VPI-5 open. As has been said, it had been found by others [9] that only a small amount of $\text{AlPO}_4\cdot 8$ formation was needed to produce a large drop in pore volume because the collapse tended to start at the exterior of crystals, thus rapidly sealing up the structure. If the presence of dye could prevent this, even in cases where there was a small amount of $\text{AlPO}_4\cdot 8$ formation, then it would be a very interesting result.

Experimental. The experiment was to use the dye / VPI-5 sample which other tests indicated had the most stabilised VPI-5 framework: waxoline orange 3GPFW was the dye which was chosen. The measurement of micropore volumes was to be done at I.C.I. Wilton. This followed initial work at Edinburgh to determine the best ways to prepare the samples.

Measurements were to be carried out on two samples:

- a) A sample of DPA-VPI-5, with only water in the channels.
- b) A sample of DPA-VPI-5 loaded with waxoline orange 3GPFW.

Prior to the first measurements the samples were to be dried by evacuation at 10^{-5} torr for 48 hours. Full nitrogen isotherms, both desorption and sorption, were then to be measured.

The next step was to be calcination at 750°C in a flow of dry air, followed by measurement of a further full nitrogen isotherm.

It was expected that this work would show a high initial pore volume in the VPI-5 blank, falling to a low pore volume after heating, due to $\text{AlPO}_4\cdot 8$ formation. To contrast with this it was hoped that the dye / VPI-5 complex would initially have a low pore volume due to the presence of dye in the pores. After heating the dye would be calcined out but the VPI-5 framework would have remained intact, thus there would then be a large pore volume, similar to that initially measured for blank VPI-5. Such a result would show the effectiveness of dye as a structural scaffold during the crucial period of water loss. If not seen it would show that the VPI-5 framework was not that easy to stabilise.

Results. A large quantity of stabilised VPI-5 needed to be made in order to carry out this study. When samples were first being prepared it had not yet been realised that longer heating times in the FEP might be detrimental. This led to several poor batches of products as times greater than seven days were tried. However, with the experience of the work described in section 5.5 a sufficient quantity of well-stabilised VPI-5 was produced.

A stabilised VPI-5 / waxoline orange 3GPFW sample and a blank VPI-5 sample were sent for analysis. Unfortunately there was a problem with the equipment at I.C.I. plc. so the sample was sent back to Edinburgh for calcination. It was lost in transit and so the chance to collect a key piece of data was missed. It therefore cannot be said whether waxoline orange 3GPFW stabilised VPI-5 so well that the structure remained fully intact, with no loss of pore volume, upon short exposure to high temperature, as experienced in calcination.

5.8 Overall Conclusions

A route was found by which large amounts of dye could be sorbed into VPI-5, without the formation of $\text{AlPO}_4\text{-8}$.

Several dyes were seen to act as structural scaffolds which prevented the conversion of VPI-5 to $\text{AlPO}_4\text{-8}$ in whole or in part.

It was possible to remove almost all sorbed dye from intact VPI-5, with subsequent loss of the thermal stability of the framework.

Conversely use of appropriate conditions could also lead to the entrapment of large amounts of dye inside partially collapsed VPI-5.

Enhanced photostability could be conferred upon at least one dye when encapsulated in VPI-5.

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Chapter 6

The Sorption of Dyes into Zeolites

6.1 Introduction

Some experiments were carried out in order to attempt to get dyes into molecular sieves other than VPI-5. The materials used were of two structure types; faujasite (FAU) and pentasil (MFI). Three FAU materials were used: the sodium forms of zeolites X and Y (Na-X and Na-Y) and the hydrogen form of dealuminated zeolite Y (H-DY). Zeolite ZSM-5 and its all-silica analogue silicalite were the two materials with the MFI structure that were used.

The general aims were the same as those which drove work with VPI-5. That is the discovery of methods by which large quantities of dye could be sorbed or encapsulated into the molecular sieves and subsequent analysis for novel effects.

There were of course differences in the way that the task was approached, due to the differences between the structures. FAU materials, for example, have cages of nearly 12Å in diameter, thus similar in size to the channels of VPI-5. However the entrances to these cages are only 7.8Å in diameter. Even smaller are the channels of the MFI materials which are only about 5.5Å in diameter, although they are interconnected which leads to relatively large voids at the intersections. The structures of faujasite and of the pentasil ZSM-5 were shown in Figures 1.1 and 1.2. The pore sizes meant that compared with VPI-5 the choice of dyes was greatly restricted.

On the positive side, all of the molecular sieves used in this chapter have high thermal stability [1,2] thereby eliminating the major problem that dogged VPI-5 work. The zeolites are also synthesized from alkaline rather than acid solutions, unlike VPI-5. Dyes tend to be more resistant to alkali than to acid and so many of them can survive dissolution in the alkaline synthesis gels. As will be seen in Section 6.3 dyes were put into the appropriate synthesis gels for ZSM-5 and silicalite in the hope that they would be trapped in the structures during crystallisation. This meant that larger dyes

could be used than could fit into the channels of MFI structures. Unfortunately it also meant that the chosen dyes would have to be capable of templating the MFI structure, for otherwise crystallisation would not take place.

It was believed that the pores of FAU structures were large enough to enable selected dyes to be sorbed into already synthesized crystals. A feature of the FAU structures was that, being zeolites, they all had aluminosilicate frameworks, even dealuminated Y. As was said in Chapter 1 these frameworks are charged therefore requiring cations, in this case sodium or hydrogen. The number of cations varied as the Al : Si ratio varied and as was also said in Chapter 1 the ratio was approximately 1.5 for Na-X, whilst for H-DY it was 60. The different cations and different Al : Si ratios were likely to cause different interaction between the dyes and the three FAU materials.

Unlike VPI-5, there have been several previous studies on the sorption or incorporation of dyes into zeolites and so there were a number of references from which to get ideas [3,4,5,6,7]. The most useful of these was the work of Schulz-Ekloff *et al* [5] which detailed methods of introducing:- cationic dyes by ion-exchange; neutral dyes by sorption from solvents or gas-phase absorption; and all types of dye by inclusion during crystallisation. Several of these methods were followed during the course of this work.

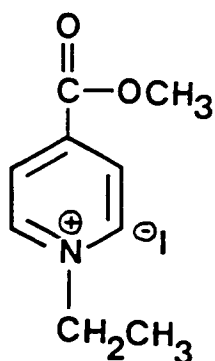
6.2 Work with FAU Structures

6.2.1 Uptake of Solvatochromic Dyes

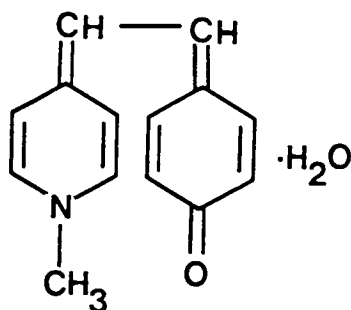
There was, as has been said, much interest in 'chromic dyes. Two solvatochromic dyes were obtained which appeared from modeling to be suitably sized to sorb into the faujasites. Figure 6.1 shows the structures of the two dyes and gives their full names, they will be referred to in the text as S1 and S2.

Uptake of the dyes from solutions was attempted, the solvents used were distilled water, ethanol, and hexan-1-ol. The idea was to have the dyes in solvents of differing polarity. Dye concentrations were 5×10^{-3} M. 10 ml of dye solution was added to 0.25 g of zeolite. On the assumption that one dye molecule could fit into each cage then 10 ml of 5×10^{-3} M dye solution would contain approximately a threefold excess over the amount of dye required to saturate 0.25 g of faujasite. At such loadings the saturated structures would contain 1 - 2 % w/w dye.

Figure 6.1
Structures and full names of the solvatochromic dyes, S1 and S2



1-ethyl-4-(methoxycarbonyl)-pyridinium iodide (S1)



4-[(1-methyl-4-(1H)-pyridinyldene)ethylidene]-2,5-cyclohexadien-1-one hydrate (S2)

Prior to contact with the dye solutions, preweighed 0.25 g portions of the zeolites were placed into bottles and dried at 95°C for 12 hours. They were allowed to cool for about a minute before 10 ml of dye solution was added. This allowed the zeolites to cool slightly, although they were still warm when the dye solutions were added. The bottles were stoppered and left to stand for 5 days, after which the zeolites were recovered by filtration. Filtered solids were washed with a small amount of the appropriate solvent to remove any surface dye, then left to dry in air. The colours of both solutions and solids were noted.

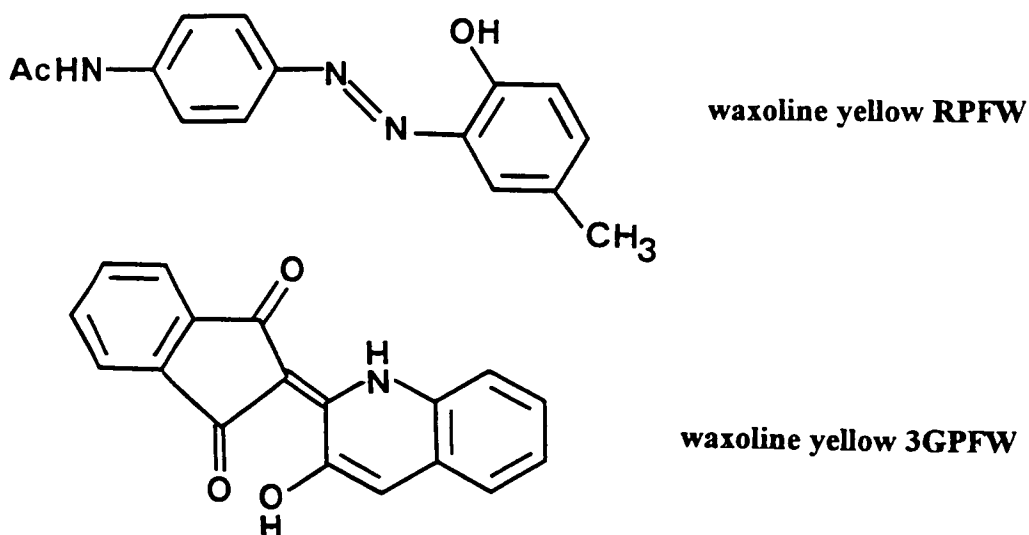
Those samples which had been contacted with aqueous and ethanolic dye solutions were equilibrated to constant humidity over saturated NaCl solution and analysed by thermal analysis. The samples which had been contacted with solutions of dye in hexan-1-ol remained strongly smelling of hexan-1-ol even after two months of sitting open to the atmosphere at 24°C. For that reason no further work was done on those samples as any interaction between dye and zeolite was likely to be affected by the solvent.

As can be seen from Figure 6.1, dye S1 was an ionic dye. Modeling had shown that the crown ether 15-crown-5 was probably too large a molecule to fit into Na-X or Na-Y. Since this crown ether can sequester Na⁺ some attempts were made to use it to aid the sorption of S1 into those zeolites. The idea was that as 15-crown-5 captured any Na⁺ which left Na-X or Na-Y then the cationic part of S1 would be attracted into the framework.

6.2.2 Uptake of ICI Dyes

Two of the ICI dyes were judged to be small enough to pass through the pores of FAU, they were waxoline yellow 3GPFW and waxoline yellow RPFW, whose structures are shown in Figure 6.2.

Figure 6.2
Structures of waxoline yellow RPFW and waxoline yellow 3GPFW



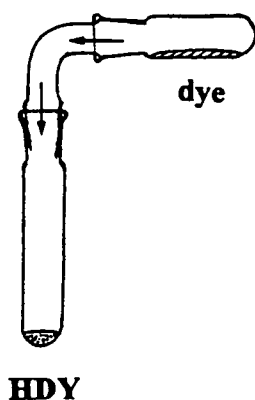
The method used to effect sorption was similar to that used in section 6.2.1. The difference was that the solvents used were ethanol and acetone. That was because neither dye was soluble in water, whilst hexan-1-ol suffered from its lack of volatility. With the solvents which were used it did not prove possible to get 5×10^{-3} M solutions of waxoline yellow 3GPFW as its solubility was too low. The undissolved solids were recovered by filtration, dried and weighed. From that it was estimated that the maximum possible concentrations of this dye were 2×10^{-3} M in acetone and 4×10^{-4} M in ethanol. There were no such problems with waxoline yellow RPFW.

As before the filtered, washed, and dried solids were equilibrated over saturated NaCl solution prior to thermal analysis. An attempt was also made to reduce the water content of the samples before thermal analysis by storing them over P_2O_5 in an evacuated dessicator. It was hoped that this would make weight loss due to dye more obvious.

There were also two other methods which were used to try and load waxoline yellow RPFW into H-DY:

- In the setup shown in Figure 6.3, dye and H-DY were heated at 140°C for 4 days. The H-DY had first been dried for 3 hours at that temperature in an unstoppered tube. The idea was that heavier than air dye vapour would fall onto the zeolite and be absorbed.
- H-DY (0.5 g) was refluxed for 7 hours in a 2.5×10^{-3} M solution of waxoline yellow RPFW in toluene. A Dean and Stark trap was attached to trap any off-coming water. The recovered zeolite was boiled in water to try and remove adhering toluene without removing any sorbed dye.

Figure 6.3 Apparatus used to attempt sorption of waxoline yellow RPFW vapour into HDY



6.2.3 Results

S1. The colours of the solids and solutions at the end of the experiment are given in Tables 6.1 and 6.2.

Table 6.1 Colours of the filtered zeolites after recovery from solutions of S1 in different solvents.

	Na-X	Na-Y	H-DY
Water	White	White	Pale Yellow
Ethanol	White	White	Pale Yellow
Hexan-1-ol	White	White	Pale Yellow

Table 6.2 Colours of the solutions of S1 in different solvents after contact with different zeolites.

	Na-X	Na-Y	H-DY	Colour of Original Solution
Water	Clear	Clear	Clear	Faint Yellow
Ethanol	Faint Yellow	Clear	Yellow	Yellow
Hexan-1-ol	Yellow	Light Yellow	Yellow	Dark Yellow

Figures 6.4 to 6.6 show the thermal analysis results for the samples of zeolites which were immersed in solutions of S1 in different solvents. The amounts of sorbed dye, as weight percentage, are given on the figures.

Figure 6.4 TGA curves to show the uptake of S1 into 13X

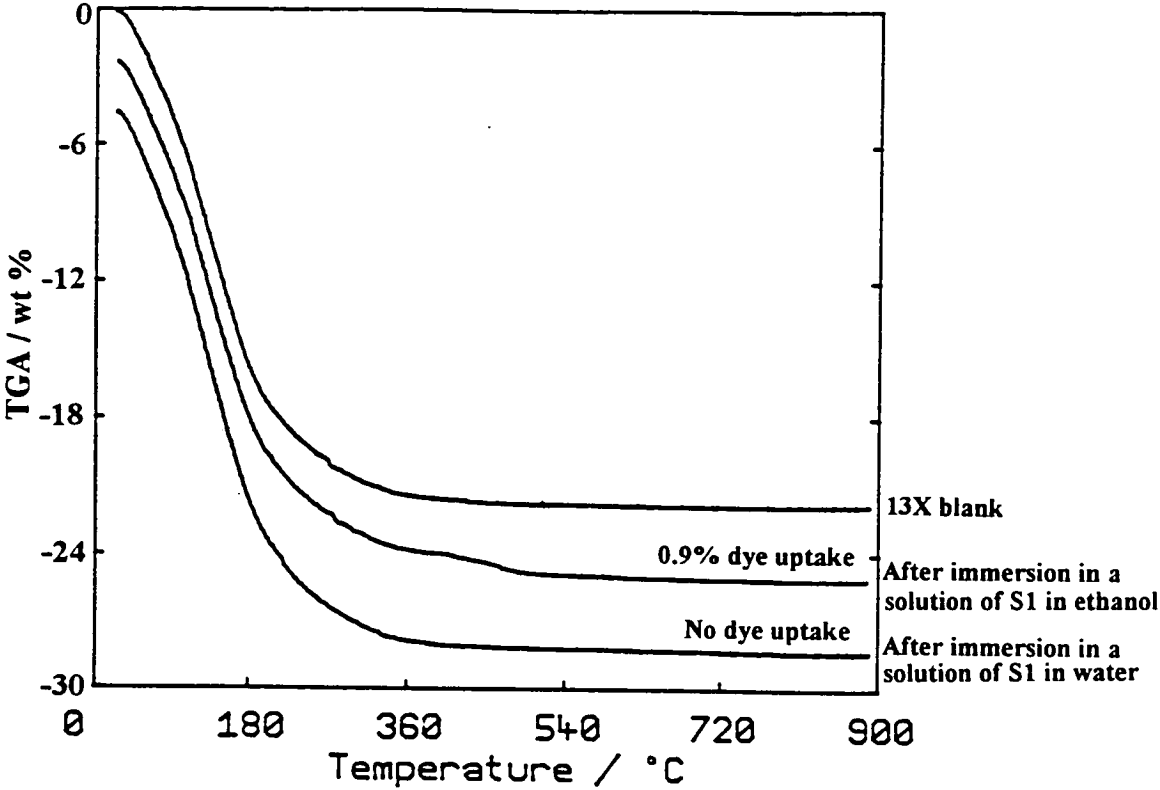


Figure 6.5 TGA curves to show the uptake of S1 into NaY

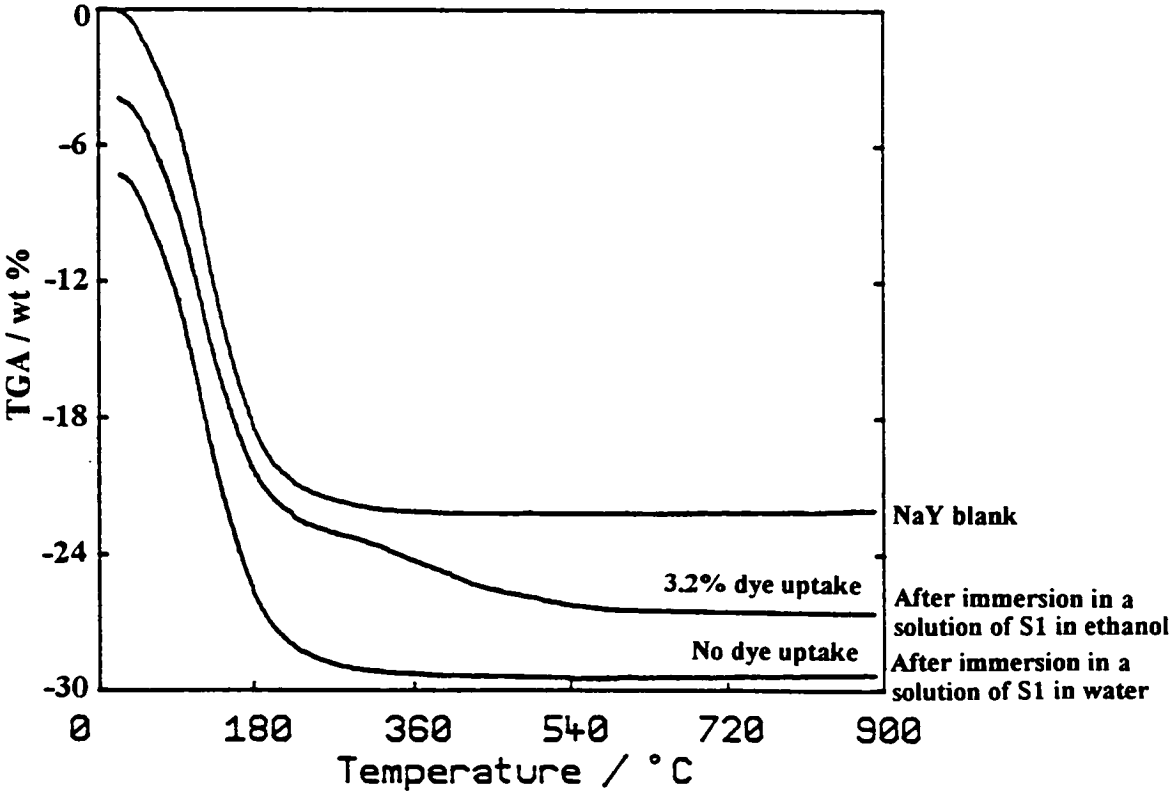
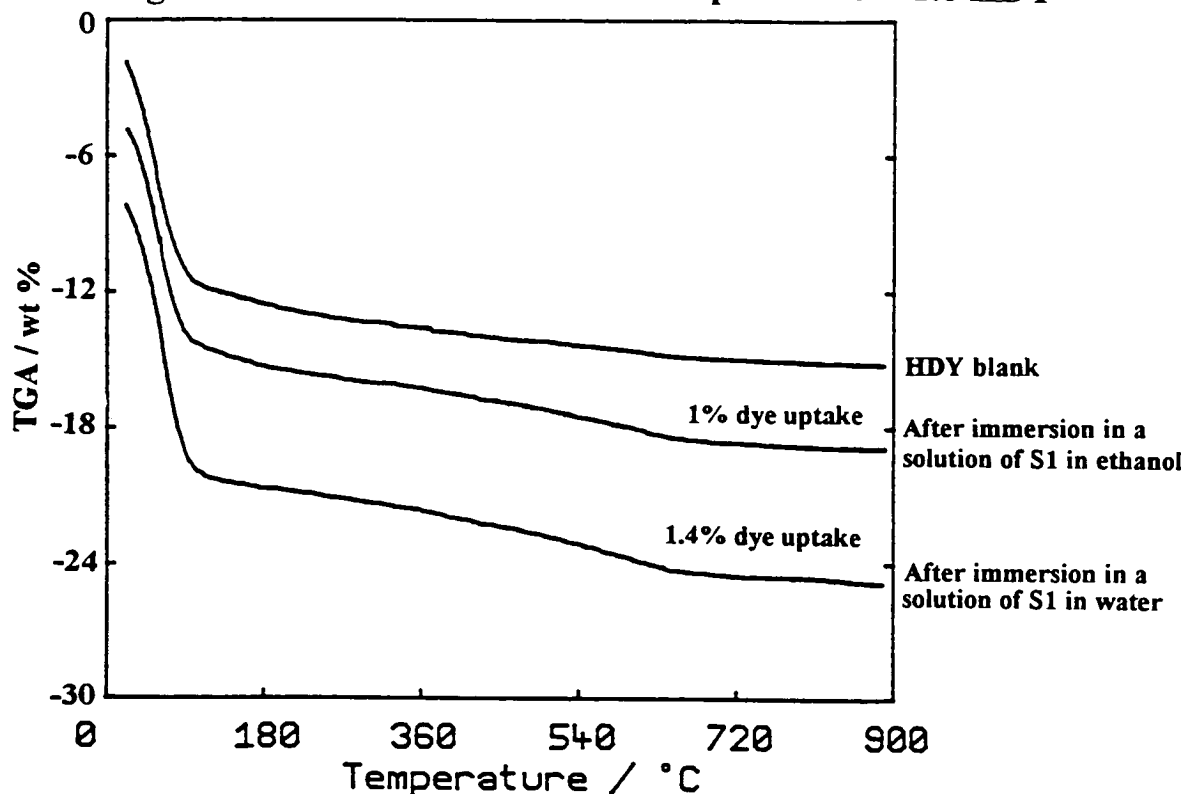


Figure 6.6 TGA curves to show the uptake of S1 into HDY



Viewed together the results indicated the following:

No significant quantities of S1 were sorbed into Na-X or Na-Y from water, for the thermal analysis shows no material to be present. There was however some interaction between those two zeolites and the dye solutions as the solutions lost their colour.

A significant amount of S1, approximately 1.4% w/w, was sorbed into H-DY from aqueous solution. This was indicated by the colour of the recovered zeolite and by its thermal analysis profile.

From ethanol solution there was clearly uptake of S1 into all of the zeolites. TGA suggested that uptake was highest into Na-Y, at around 3.2% w/w. This level of uptake is equivalent to greater than one molecule per unit cell. The colours of the solutions would appear to support this finding, as that solution into which the Na-Y had been immersed was decolourised, whilst the other two remained yellow.

Despite evidence that they had sorbed S1, no samples of Na-X or Na-Y became coloured. The reason for this is thought to be that sorption of S1 into those zeolites

was by ion exchange of Na^+ for the cationic part of S1 and that the anion Γ left behind in solution was necessary for colouration. Further evidence for the mechanism of sorption being ion-exchange came from the use of 15-crown-5: This did not lead to greater dye uptake, which would have been expected if there had been no ion exchange thus far.

It is thought that a different sorption mechanism operated for HDY: the less polar framework of HDY, with its fewer cations, attracted the whole of the S1 molecule into itself. If Γ was required for colouration then this would also explain why those samples were coloured when 13X and NaY were not.

It did not prove possible to obtain anything other than shades of yellow when S1 was sorbed into H-DY, thus no novel effects had been seen. The work had however been successful in showing that S1 could fit inside the FAU structure and had achieved very high loadings of greater than one molecule per unit cell, which is near saturation.

S2. The colours of the solids and solutions at the end of the experiment are given in Tables 6.3 and 6.4.

Table 6.3 Colours of the filtered zeolites after recovery from solutions of S2 in different solvents.

	Na-X	Na-Y	H-DY
Water	White	Pale Orange	Yellow
Ethanol	Pale Orange	Orange-Yellow	Yellow
Hexan-1-ol	Orange	Orange	Yellow

Table 6.4 Colours of the solutions of S2 in different solvents after contact with different zeolites.

	Na-X	Na-Y	H-DY	Colour of Original Solution
Water	Orange	Orange	Pale Yellow	Orange
Ethanol	Red	Red	Orange	Red
Hexan-1-ol	Red	Pale Red	Pale Yellow	Dark Red

Figures 6.7 to 6.11 show the thermal analysis results for the samples of zeolites which were immersed in solutions of S2 in different solvents. Again, the amount of sorbed dye is stated on the figures.

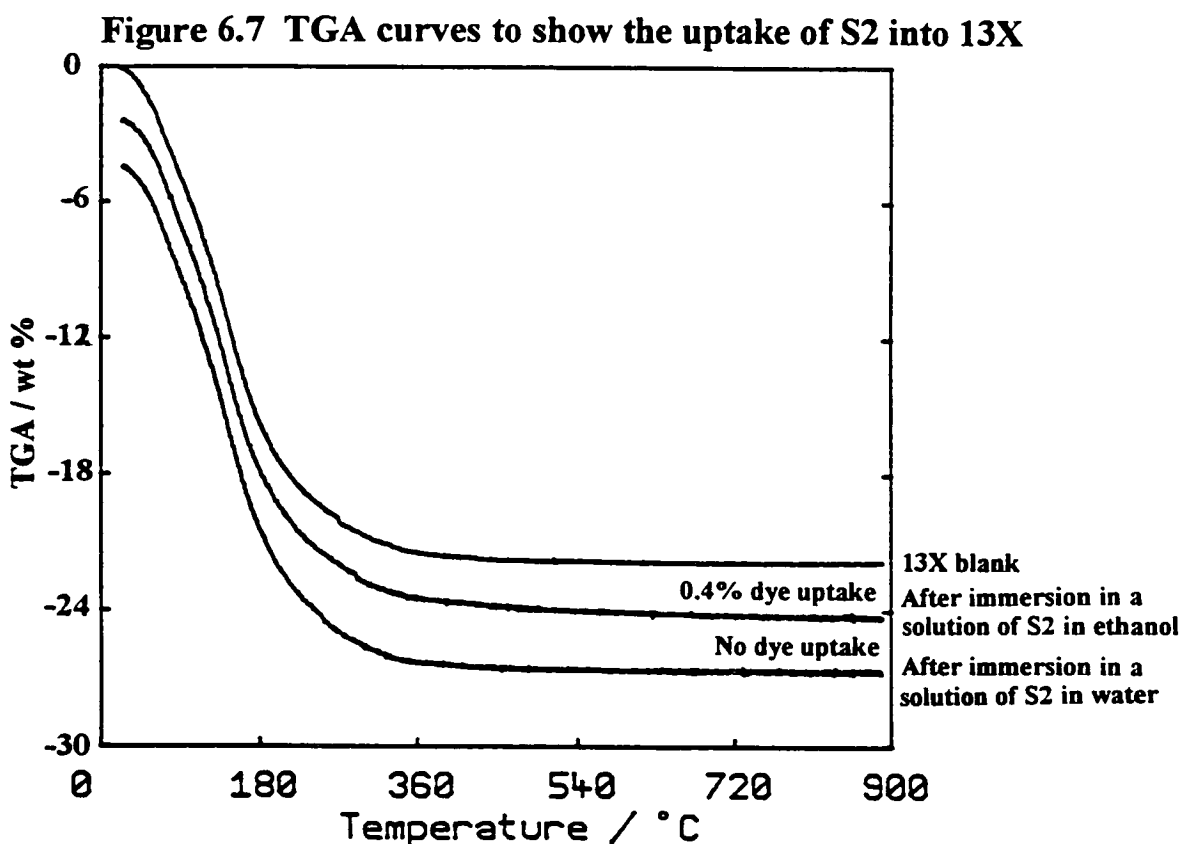


Figure 6.8 TGA curves to show the uptake of S2 into NaY

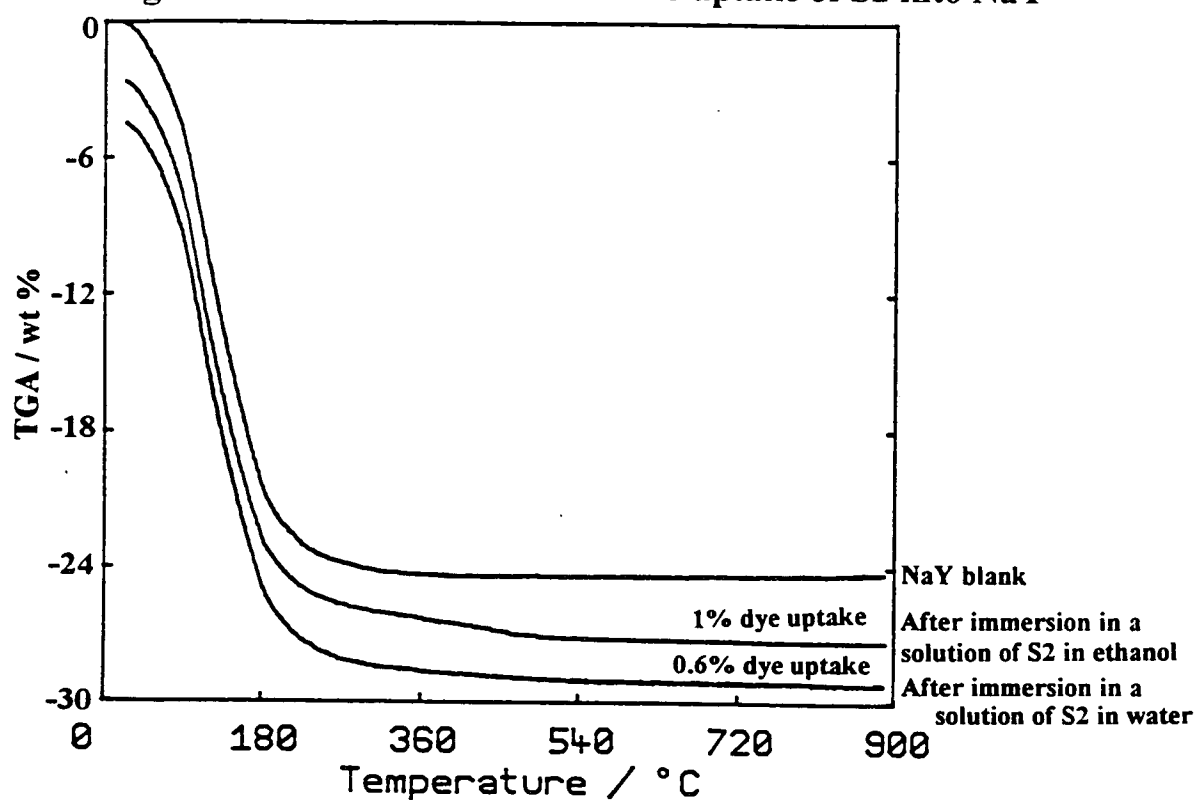
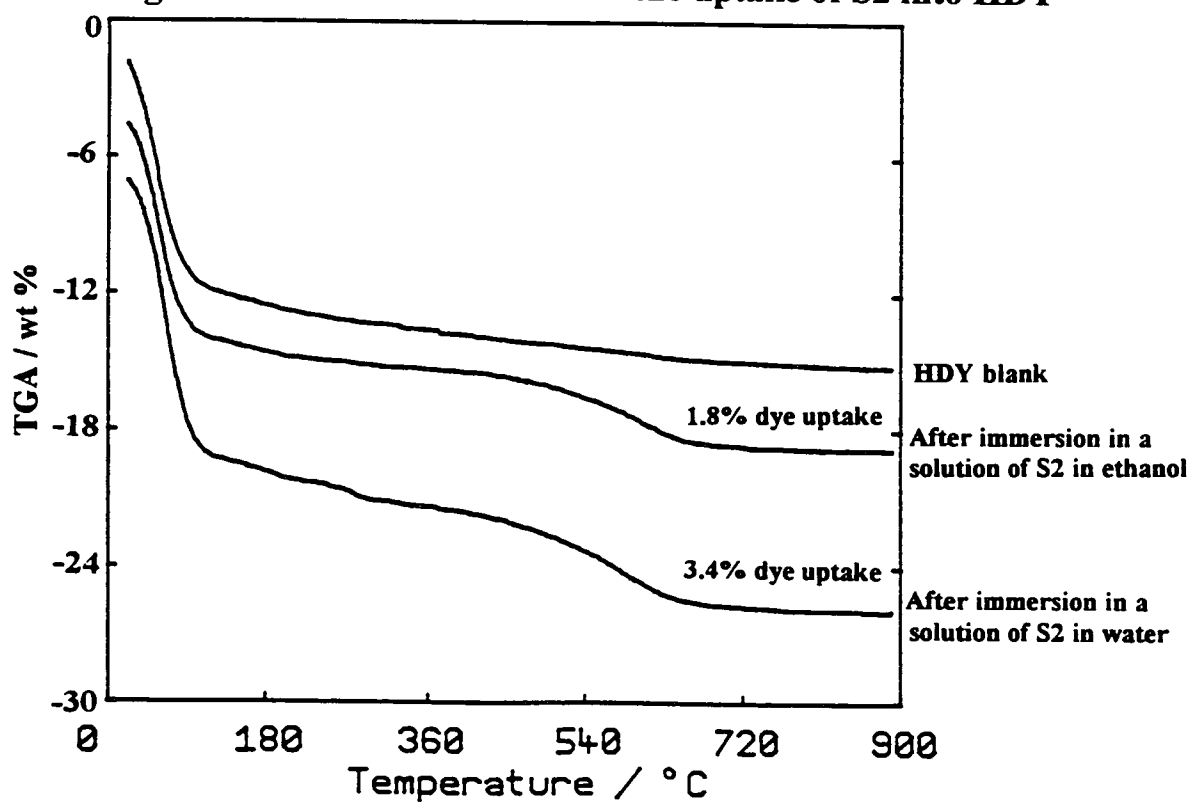


Figure 6.9 TGA curves to show the uptake of S2 into HDY



The results for S2 were fairly clear cut: it appeared to be strongly sorbed into H-DY, weakly into Na-Y, and barely at all into Na-X. This would suggest that S2 generally prefers less polar environments.

The colours seen in sorbed S2 were still strongly dependent upon solvent, and more especially upon water. The pale orange sample of S2-loaded Na-X became yellow when heated, then returned to its original colour when left to cool and rehydrate in air. The opposite effect was seen in the sample in which S2 had been sorbed into H-DY from ethanol: it became orange when heated then returned to yellow. These interesting results showed that the framework exerts an influence on the colour of S2 and that, although water affects the colour at least as much, it suggests that it may be possible to use S2 to investigate the polarity^{of} zeolite frameworks.

Thus some interesting effects were seen, it was shown that S2 could fit inside the FAU framework and it was shown that it was possible to achieve very high loadings, again near saturation, of S2 in H-DY.

Waxoline Yellows 3GPFW and RPFW. Work with waxoline yellow 3GPFW was unsuccessful and so efforts concentrated upon waxoline yellow RPFW. After initial contact of all three zeolites with solutions of waxoline yellow RPFW there appeared to have been very little or no uptake of dye;

The samples of Na-X and Na-Y remained white and their TGA traces were indistinguishable from the starting materials, therefore it was concluded that no sorption had taken place.

The samples of H-DY were pale yellow and so it appeared that some dye had been sorbed. The faint colour suggested that the quantities were very low and this was backed up by thermal analysis. The TGA traces indicated that the amount of sorbed dye was less than 0.5% w/w.

It was because of the very low quantities of sorbed dye that attempts were made to reduce the water contents prior to further thermal analysis. Desiccation did not improve the quality of thermal analysis data but it did lead to a very interesting result. That result was that the samples of H-DY which contained waxoline yellow RPFW turned pink when desiccated. Furthermore rehydration caused the dye to become yellow again. Waxoline yellow RPFW was not an acknowledged solvatochromic dye and yet it seemed that such behaviour had been triggered by absorption into H-DY.

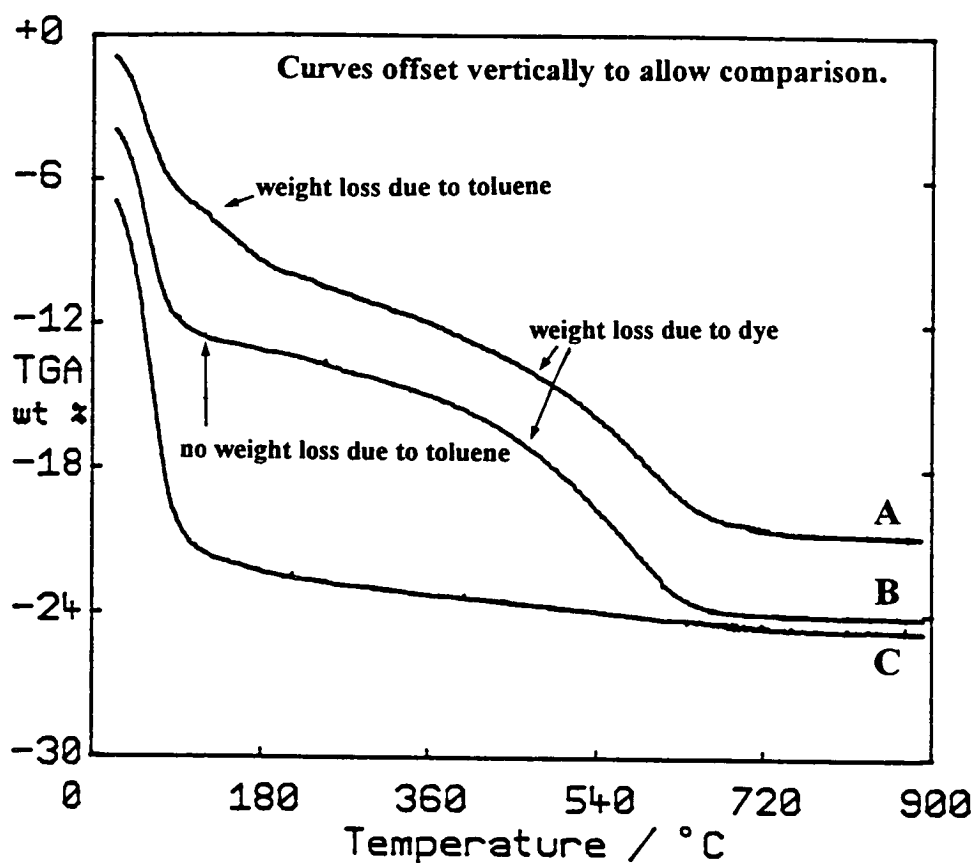
Desiccation had originally been carried out at room temperature over P_2O_5 , but it was

found that heating the sample had the same effect. Even with heating there appeared to be no limit to the number of times that the colour change could be cycled.

Attempts were made to find out if any other materials could cause the same effect upon waxoline yellow RPFW. Dye was desiccated on its own, with silica, with alumina, with ZSM-5, and as a physical mixture with H-DY. In none of these cases was solvatochromic behaviour triggered. Thus it was concluded that the sorption of waxoline yellow RPFW into the hydrogen form of dealuminated zeolite Y had led to the formation of a complex whose colour was sensitive to water. A possible reason is that the absence of water allowed the dye to interact more strongly with the hydrogen ions. This would expose the dye to a more polar environment and it has been shown that many dyes undergo positive solvatochromism when their solvent polarity increases [8], that is they undergo a bathochromic shift such that they absorb longer wavelength light.

As was described, attempts were also made get higher loadings of dye. Heating waxoline yellow RPFW and H-DY in a tube did not work, the vapour pressure of the dye must not have been high enough. Putting H-DY into a refluxing solution of dye in toluene, with a Dean and Stark trap attached did work. The recovered solids were a much darker yellow, indicating the presence of larger quantities of dye. There was, however, much uptake of toluene as well as dye and so it was difficult to estimate the level of dye uptake from TGA data. Figure 10 shows the TGA traces, they show a large amount of sorbed material and also that by boiling the zeolite in water much toluene was removed. The complex was seen to retain its solvatochromic abilities with higher loadings of dye.

Figure 6.10 TGA curves showing uptake of waxoline yellow RPFW by dealuminated zeolite Y



- A. HDY heated with a solution of dye in toluene**
- B. Sample A refluxed with water**
- C. Blank HDY**

6.3 Synthesis of MFI in the presence of Dyes

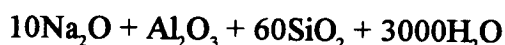
Few dyes are small enough to fit inside a zeolite with channels as small as those found in the MFI structure type. A number of dyes were, however, thought to be capable of encapsulation if, as mentioned above, they could be incorporated into the crystals during synthesis. To this end the synthesis of ZSM-5 and silicalite was attempted, with dye in the role of template.

ZSM-5 is a fairly hydrophobic zeolite and Silicalite a very hydrophobic molecular sieve. Since some of the dyes to be used were also hydrophobic it was hoped that they would be taken up during synthesis by one, or both of the structures.

Standard reaction mixtures were used for both silicalite and ZSM-5. Also for ZSM-5, a novel reaction mixture was used, which had been reported by Nee [9] and which was referred to by him as the scavenging reaction. This was because of its extreme sensitivity to any amount of organic which could template ZSM-5 formation. Thus if any of the dyes were going to be suitable templates, this would be the reaction mixture from which they would most easily form ZSM-5 and thus be incorporated into its channels.

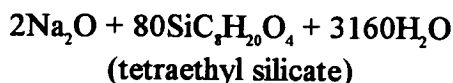
6.3.1 ZSM-5 and Silicalite Syntheses from standard preparations

The ZSM-5 reaction mixture was of the composition;



to which was added either 2 or 5 parts dye. No other template was added to the synthesis gel. The dyes used in these reactions were the solvatochromic dyes S1 and S2 which were used in section 6.2. Reaction mixture was loaded into 10cm melting-point tubes, which were sealed and heated at 130, 140, and 150°C for a range of times.

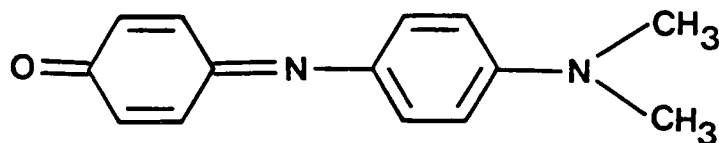
The Silicalite reaction mixture was of the composition:



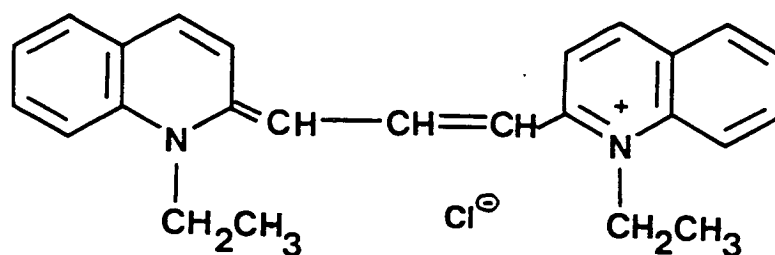
To which was added 3 or 5 parts dye, again no other template was added to the gel. Reactions were initially carried out in melting-point tubes under the same conditions as were used for ZSM-5 synthesis, with S1 used as template. Subsequently S2 and

also the dyes pinacyanol chloride (quinaldine blue) and N,N-dimethylindoaniline were used. The structures of the additional dyes are shown in Figure 6.11. As well as using melting point tubes, these reactions were also done in TOMs, with 1.5 ml of mixture put into each TOM.

Figure 6.11 Structures of N,N-dimethylindoaniline and quinaldine blue



N,N-dimethylindoaniline



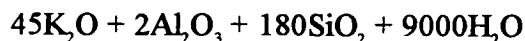
pinacyanol chloride (quinaldine blue)

The contents of tubes were recovered by the use of pistons which fitted snugly inside them. Amorphous material present in the recovered products needed to be separated from the crystals, as it could dry into hard lumps from which the crystals were inseparable. The tube contents were slurried into water, so as to try and dissolve as much amorphous material as possible. Since crystals tended to settle faster than amorphous material, the slurries were then carefully decanted..

For most samples, enough solids were recovered to enable XRPD analysis to be carried out using special backing plates which were cut from a silicon single crystal. Samples were ground and sprinkled onto the plates, with a thin layer of silicone grease used to ensure that they remained in place. The plates gave only one small diffraction line in the region of interest, at $38.2^\circ 2\theta$.

6.3.2 ZSM-5 Synthesis from the Scavenging Reaction

The scavenging reaction used a gel of the composition;



It was found by Nee [9] that this reaction was extremely sensitive to the presence of any material which could cause ZSM-5 formation, be that seeds or a suitable organic template. This made the reaction very useful for testing that reaction vessels were scrupulously clean and, more importantly, for testing to see whether materials could template ZSM-5 formation. For this reason it was hoped that if any of the dyes did have any ability to template ZSM-5, they would do so if added to the scavenging gel, thus producing encapsulated dye. All of the dyes used in silicalite syntheses were used with the scavenging gel, added to the above composition at the level of 10 parts dye. Reaction gels were loaded into melting-point tubes and heated at 150°C for up to nine days.

6.3.3 Results for Standard Syntheses.

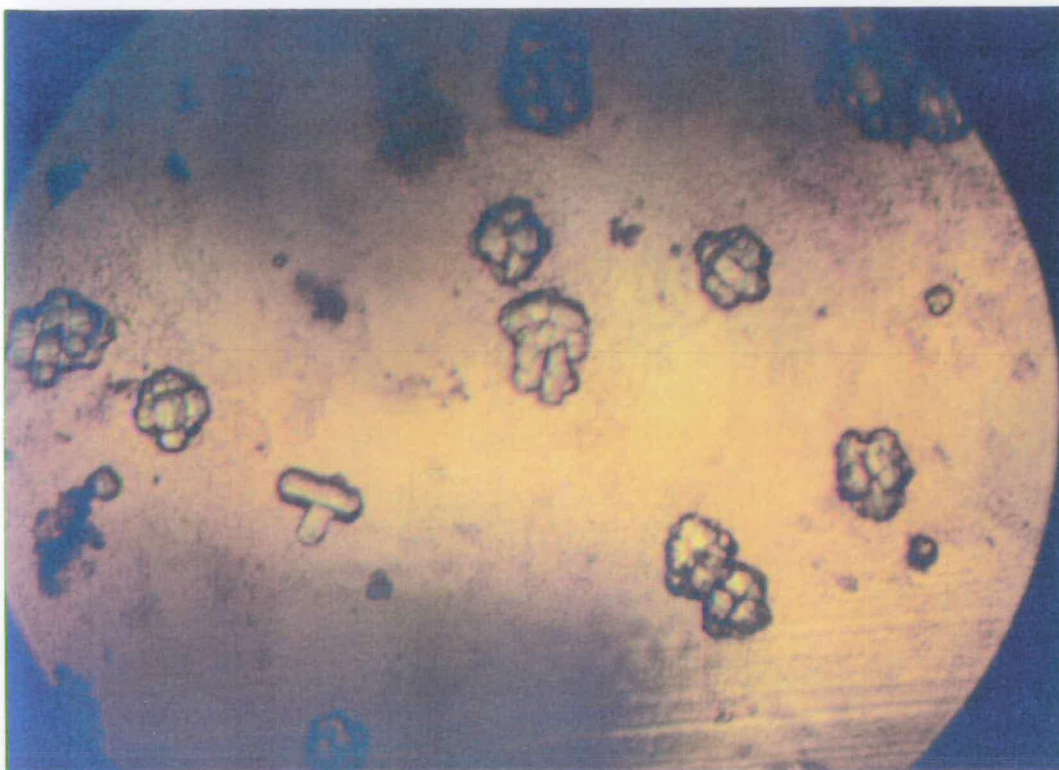
ZSM-5. Analysis, by optical microscope, of the contents of the melting point tubes used for attempts at ZSM-5 synthesis failed to find any ZSM-5 crystals, even after 28 days.

Silicalite. Silicalite syntheses on the other hand did yield some crystals. These came from syntheses in melting-point tubes with S1:

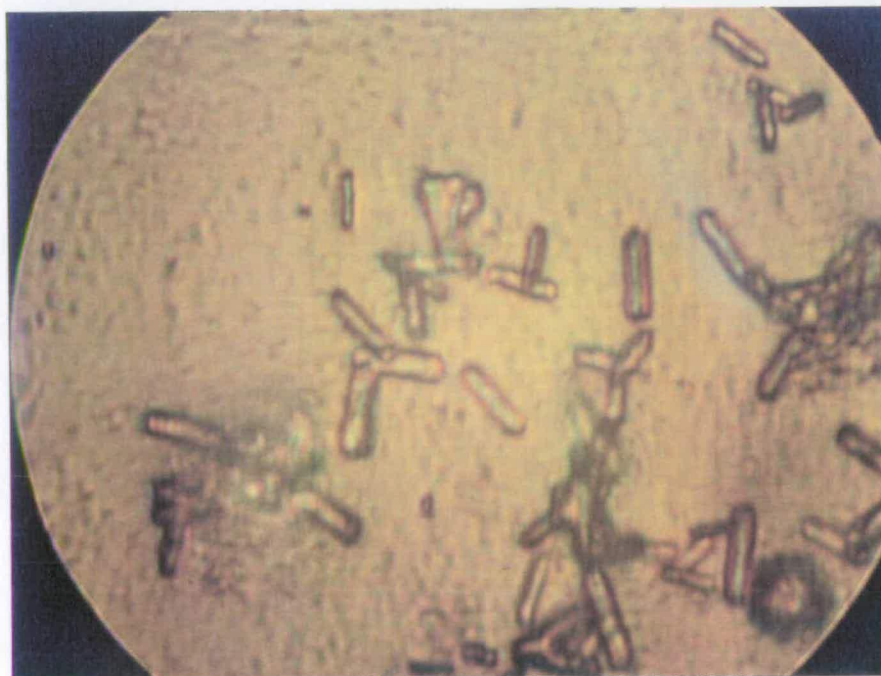
After 14 days at 150°C, a number of crystals, approximately 60µm long and of the typical silicalite shape, were seen. They were seen in gels with both 3 and 5 parts dye in them, however the dye concentration appeared to affect the crystals. Most of those in the reaction which contained 5 parts dye were single, whilst in the mixture which contained 3 parts dye most of the crystals appeared to be multiply twinned, as shown in Figure 6.12.

The differences in the crystal habits seemed to indicate that S1 was having an effect on the formation of silicalite. It should be noted, however, that the crystals were only a small proportion of the tube contents: most of the contents were gel or particles too small or too densely packed to identify as crystalline or amorphous. Also, the products varied along the length of the tubes, often with very defined areas for different products.

Figure 6.12 Products from Silicalite syntheses with S1



3 parts dye in synthesis gel. Multiply twinned crystals.



5 parts dye in synthesis gel. Mainly single crystals.

In the 140°C reactions it was not until after 21 days that some small (25µm) silicalite crystals were seen. At no time were any crystals spotted in the 130°C reaction.

The results from XRPD analysis of the samples are given in Table 6.5.

Table 6.5. Attempts to use S1 to synthesize Silicalite.

Conditions	7 days	14 days	21 days	28 days
130° / 3dye ^a	Amorphous	Am	Am	Am
130° / 5dye	Am	Am	Am	Am
140° / 3dye	Am	Am	Am / (MFI) ^b	Am/(MFI/ M ^c)
140° / 5dye	Am	-	-	-
150° / 3dye	Am	MFI/ (M /Am)	MFI / M / Am	-
150° / 5dye	Am	Am/ M/ (MFI)	-	-

^a Proportion of dye in reaction mixture, *vide ultra*.

^b Parentheses indicate a minor component.

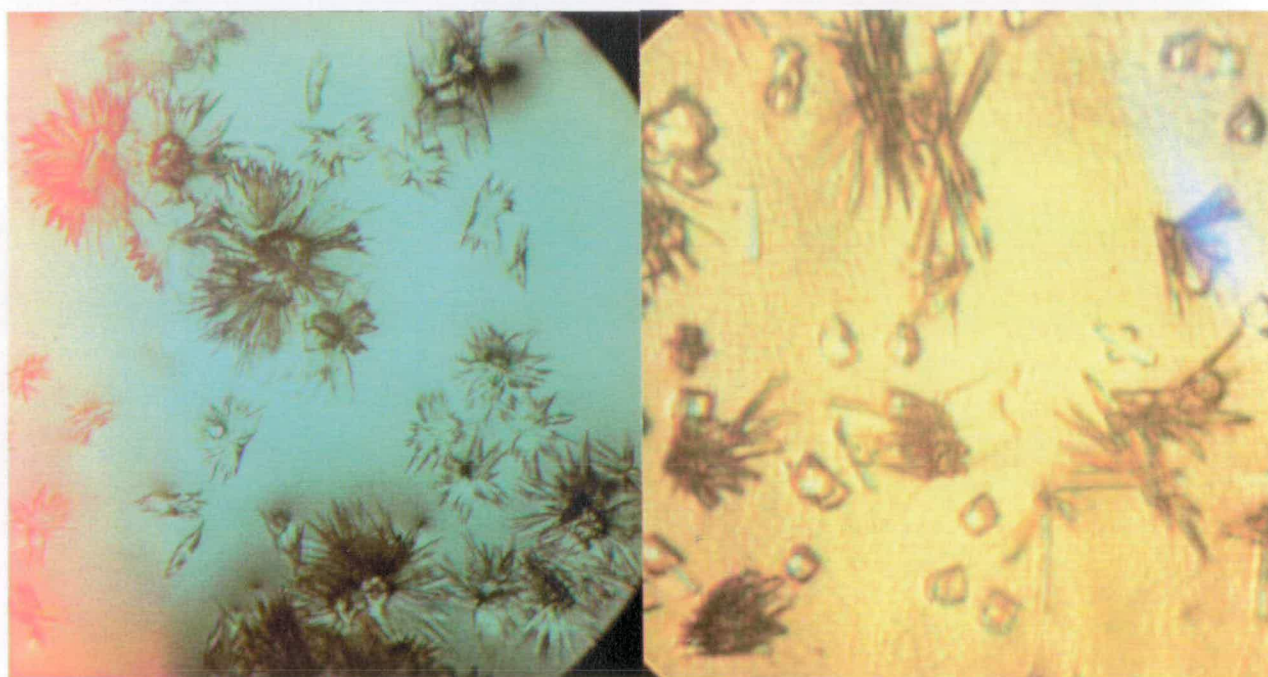
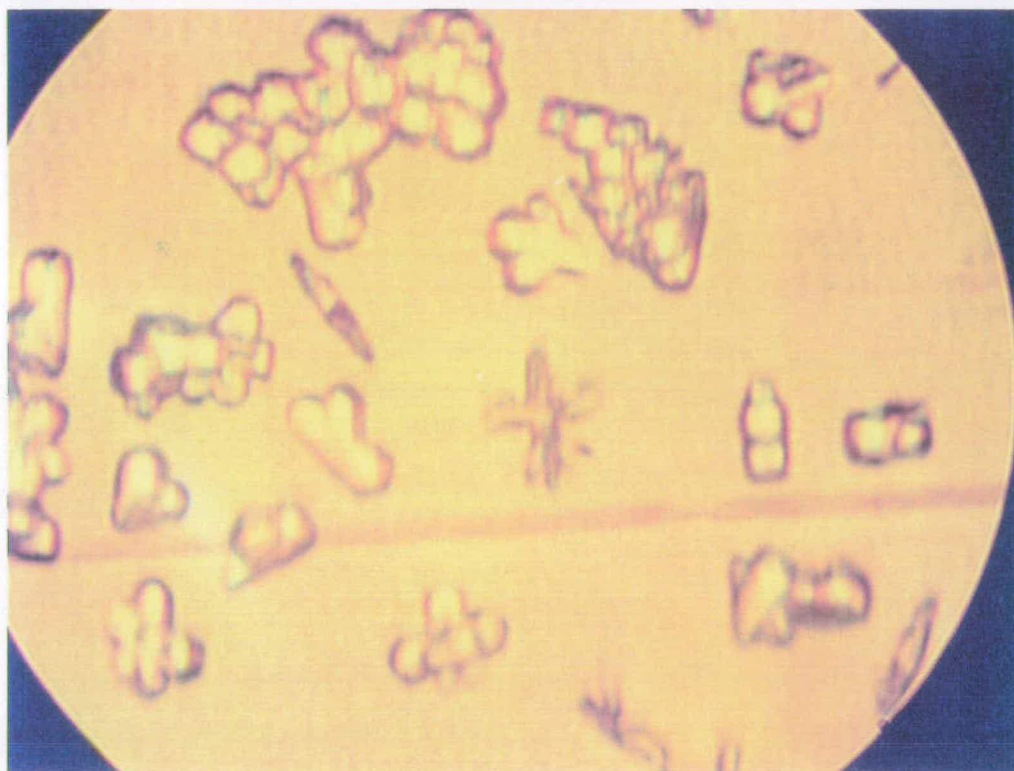
^c M = Magadiite.

The results were unfortunately incomplete because several tubes burst. It seemed, however, that the best results, in terms of purity of product, were those from the mixtures heated to 150°C and which contained 3 parts dye. Further silicalite syntheses therefore used 3 parts dye and were done at 150°C.

These further attempts were those which used TOMS and also other dyes as well as S1. Crystals of the correct shape for MFI were seen to form for every dye, although this was only in the melting-point tubes and, as Figure 6.13 shows, other crystal habits were also seen.

XRPD analysis of recovered products showed the presence of MFI for all dyes except N,N-dimethylindoline. The amounts formed were, however, very low and the dense phase magadiite was usually seen also. Another dense phase, Kenyaite, was seen in several reactions which contained S2.

Figure 6.13 A variety of crystals seen in the products from silicalite syntheses.



From Figures 6.12 and 6.13 it can be seen that those crystals of MFI which did form were colourless, despite the fact that the dyes appeared to have remained intact in most of the syntheses. Thus it seems unlikely that they contained significant quantities of dye.

No syntheses which were carried out in TOMS produced any crystalline material. The only exception was a control which contained ground glass: that produced a small amount of Kenyaite

6.3.4 Results from Scavenging Gel Syntheses

Only S1 and pinacyanol chloride dissolved readily in the scavenging gel, the other dyes only dissolved partially. For those dyes that did not dissolve fully, the mixtures were centrifuged and two sets of reaction vessels were set up, one set contained only dissolved dye and the other set contained both dissolved and suspended dye.

Optical microscopy showed no MFI-shaped crystals in any of the tubes, most of the contents were amorphous, although there were a variety of needles and wheatsheaves. XRPD analysis of the recovered solids failed to find any ZSM-5. The only pattern seen was that of Kenyaite, which occurred in small quantities in a few of the reactions, most especially in a blank run which contained only scavenging gel.

6.4 Conclusions

Large quantities of the two solvatochromic dyes were sorbed into FAU materials with relative ease. No novel effects were seen, but it was shown that in the absence of solvent the framework had an effect upon the colour of S2.

Waxoline yellow RPFW was successfully sorbed into the hydrogen form of dealuminated zeolite Y₄. ^{in 7 hours} This led to the formation of a water-sensitive solvatochromic complex in which desiccation caused a bathochromic shift in the absorption of the dye, which led to a colour change from yellow to pink.

It did not prove possible to use dyes to template the formation of ZSM-5 or silicalite. In those cases where the MFI structure was seen to form, visual evidence suggested that little or no dye was incorporated into the structure.

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